# University of Reading

**School of Mathematics, Meteorology & Physics**

# PETROL OR DIESEL

by

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This dissertation is a joint MSc in the Departments of Mathematics & Meteorology and is submitted in partial fulfilment of the requirements for the degree of Master of Science

I confirm that this is my own work and the use of all material from other sources has been properly and fully acknowledged.

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Duduzile Nhlengethwa

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**Abstract**

The impact of anthropogenic emissions on climate change has been an area of great concern, and the significant contribution from transportation, in particular, road transportation has been acknowledged. There has also been growing concern on the impacts of road transportation emissions on air quality and environmental health. These two areas have linkages as they are concerned with the same emissions.

This dissertation studies the impacts of the different constituents of road transportation emissions, with more emphasis on the climate impacts. The emissions are grouped into petrol and diesel emissions. After an investigation of different metrics and collection of data and costants (emission factors, emission lifetimes and perturbation times, etc.) a comparison of the emissions due to the different fuel types is made. In the absence of global disaggregated data, the United Kingdom's (UK) data for 2002 is used.

It is found that petrol vehicles give more emissions with greater impact (radiative forcing and temperature change). However diesel emissions do have a higher impact, interms of temperature change, within the first few decades.

# List of Acronyms

| | |
|---|---|
| AGTP | Absulute Global Temperature-change Potential |
| AGWP | Absolute Global Warming Potential |
| CCN | Cloud Condensation Nucleus |
| GHG | Greenhouse Gas |
| GTP | Global Temperature-change Potential |
| GWP | Global Warming Potential |
| HC | Hydrocarbon |
| HFC | Hydrofluorocarbon |
| IPCC | Intergovernmental Panel on Climate Change |
| LLGHG | Long Lived GHG |
| MTBE | Methly Tert-Butyl Ether |
| OC | Organic Carbon |
| PAH | Polycyclic Aromatic Hydrocarbon |
| PFC | Perfluorocarbon |
| PM | Particulate Matter |
| $PM_{10}$ | Particulate Matter (course), diameter less than 10 microns |
| $PM_{2.5}$ | Particulate Matter (fine), diameter less than 2.5 microns |
| $PM_{0.1}$ | Particulate Matter (ultrafine), diameter less than 0.1 microns |
| TWC | Three Way Catalyst |
| UNFCCC | United Nations Framework Convention on Climate Change |
| VOC | Volatile Organic Compound |

# List of symbols

$\lambda$        Climate Sensitivity

$\Delta T$      Transient Temperature Change

$\Delta T_{eq}$    Equilibrium Temperature Change

$\Delta F$      Radiative Forcing

C       Heat Capacity

# Chemical symbols

| | |
|---|---|
| $CO_2$ | Carbon Dioxide |
| $CO$ | Carbon Monoxide |
| $CH_4$ | Methane |
| $H_2SO_4$ | Sulphuric Acid |
| $HNO_3$ | Nitric Acid |
| $N_2O$ | Nitrous oxide |
| $NO_x$ | Oxides of Nitrogen |
| $NH_3$ | Ammonia |
| $NH_4NO_3$ | Ammonium Nitrate |
| $(NH_4)_2SO_4$ | Ammonium Sulphate |
| $OH$ | Hydroxyl free radical |
| $SF_6$ | Sulphur Hexafluoride |
| $SO_2$ | Sulfur Dioxide |

# Contents

# List of Figures

# List of Tables

# 1  Introduction

The Earth atmosphere is composed of different gases, with some liquid and particulate matter suspended in it. Some of these gases, known as radiatively active gases or greenhouse gases (GHGs), absorb longwave/thermal radiation emitted by the Earth surface and atmosphere. This process is refered to as the greenhouse effect, and keeps the Earth's lower atmosphere at temperatures suitable for the sustainability of life. Without the greenhouse effect the global average temperature would be about $-18\,°C$ (Hansen et al., 1981). Altering the composition of the atmosphere, therefore, alters the Earth's radiative budget, changing the amount of thermal radiation trapped in the lower atmosphere. Over centuries there have been changes in this composition, and hence changes in the Earth's radiative budget and climate, ranging from glacial to interglacial periods. Studies have shown a correlation between global average temperatures and the atmospheric composition of some GHGs, such as carbon dioxide ($CO_2$), methane ($CH_4$) and nitrous oxide ($NO_2$).

Since the begining of the twentieth century there has been a growing concern about human activities. These were postulated to alter the Earth atmosphere's compostion sufficiently to alter its climate. It was not until the end of the 1970s that scientists agreed that these alterations result in warming rather than cooling. Evidence has been growing in this regard, and the recent Intergovernmental Panel on Climate Change (IPCC) fourth assessment report (AR4) states that, to a 95% confidence level, observed increases in anthropogenic greenhouse gases are responsible for most of the observed increase in global average temperatures over the last 50 years (Hegerl & Zwiers, 2007). The concentrations of the greenhouse gases have increased exponentially since the begining of industrialisation. The increase varies for different gases, and also varies from source to source.

On the otherhand, particulate matter (PM) was not taken to be a serious threat to the global climate system. Concerns were held from an environmental health perspective, as it was observed to aggrevate asthma and respiratory symptoms, cause lung cancer, etc. However, there are now postulates that the effect of PM on the global climate system is of significance, with Jacobson (2002) predicting that eliminating PM, in particular black carbon and organic matter, would effectively slow down global warming within ralatively shorter time scales (3-5 years, compared to 50-200 years when reducing $CO_2$).

## 1.1   Problem

The United Nation's Framework Convetion on Climate Change's (UNFCCC) Kyoto Protocol monitors the emissions of $CO_2$, $CH_4$, $N_2O$, hydrofluorocarbons (HFCs), perfluorocarbons (PFCs) and sulphur hexafluoride ($SF_6$) from different sectors/sources. Among the considered source categories are fuel combustion from transport and fugitive emissions from fuels. Governmental reports, including National Communications under the UNFCCC reveal that for most countries emissions from transport, and in particular road transport, contribute significantly to anthropogenic emissions. For example, the American Department of Energy reports that transportation accounts for about a third of the country's $CO_2$ emissions (Energy Information Centre, 2006), while in the UK it accounts for about 22% (Avery, 2007). Other pollutants

| %                   | CO   | $NO_x$ | VOC  | $PM_{10}$ |
| ------------------- | ---- | ------ | ---- | --------- |
| Transport share     | 77.3 | 54.3   | 43.7 | 2.5       |
| Road Transport Share | 76.9 | 50.1   | 43.7 | 2.3       |

**Table 1:** Contributions of the Transport Sector to carbon monoxide (CO), oxides of nitrogen ($NO_x$), volatile organic compounds (VOC) and particulate matter with a maximum diameter of $10\mu$m ($PM_{10}$ in America, 2002 (Davis & Diegel, 2007)

apart from those monitored under the Kyoto Protocol also recieve a significant contribution form the sector. A 2002 American example is shown

in table 1. This implies that emissions from road traffic are of significance and therefore warrant further analysis. There are a number of factors that contribute to the emissions in this sector. In this project we consider the differences between petrol- and diesel-engine road vehicles, including changes with technology and time.

Alternate fuels have been left out of this study. Vehicles operating on alternate fuels are currently not enjoying the advantages of mass production, and as a result have a higher production cost, and hence a low market share Johansson (1999). For example, in 2002 Ireland's road traffic fleet consituted 100% conventional fuel (petrol and diesel) vehicles, and local production of ethanol could only replace 5.7% of the conventional fuel (Murphy & McCarthy, 2005). The cost of the alternate fuels being higher than petrol and diesel, with the exception of Brazilian bioethanol, does not make the situation any better as both the initial and operating costs are higher (Ryan et al., 2006; Johansson, 1999). Brazil is, however, unlikely to be able to produce enough biodiesel to export overseas, and even if it did, transport costs would increase its price. Murphy and McCarthy (2005) suggested that in Ireland the production cost of ethanol from waste paper could be low enough to make it a viable option. However this is dependent on having enough waste paper supply within a reasonable radius from the power plant. We can therefore safely assume that the global market share of alternate fuels will remain relatively low for at least some centuries and therefore policy decisions to fleet make-up are likely to focus on conventional fuels (petrol and diesel).

A number of studies (Johansson, 1999; Kupiainen & Klimont, 2007; Mazzi & Dowlatabadi, 2007; Palmgren et al., 2003; Romilly, 1999; Schmitz et al., 2000) have revealed that emissions from petrol and diesel engines differ substantially. It is for this reason that we find a need to understand the emission impacts of the different engine types. Such an understanding could play a significant role in policy decisions, anthropogenic emissions and air quality.

## 1.2   Aims, Objectives and Organisation of the Dissertation

The overall objective of the dissertation is to assess the relative climate impact of petrol versus diesel road transport. To achieve this objective we first compare by emission mass and then by climate impact. Ideally we use global emissions, but since global road transport emissions data is not disagregated to petrol and diesel road vehicles, we use the United Kingdom, 2002, as a case study. Even so, not all road emissions data has been disagregated, hence we use some assumptions based on previous scientific studies.

The **second section** looks at the different emissions by road transportation, considering their impacts on both climate and environmental and human health. It also considers current and future emission changes as a result of changes in policy, technology and transport demands. The **third section** defines metrics used to compare by climate impact. These are based on a simple climate model that assumes that all the net radiation into the Earth's atosphere is stored within the well mixed layer of the ocean. In **section four** a model allowing communication between the mixed layer and the deep ocean, with derivations of the atmospheric temperature change for this model. The metrics are then used to make a comparison between petrol and diesel emissions in **section five** with conclusions and areas of further work outlined in the **last section**.

# 2 Emissions

The emissions from combustion under an ideal fuel/air mixture should be carbon dioxide, water and nitrogen. However combustion is quite often not optimum, therefore giving off a whole lot more emissions than these, e.g. carbon monoxide, nitrous oxide, oxides of nitrogen, hydrocarbons, etc. The emissions can generally be grouped into particulate matter and gaseous emissions. These can be further divided as shown in figure 1.

The emissions can also be divided into direct greenhouse gases, indirect greenhouse gases and criteria pollutants. Direct GHGs act by absorbing thermal radiation emitted by the Earth's surface and atmosphere, thereby trapping longwave radiation and hence increasing the temperature of the lower atmosphere. Indirect GHGs on the other hand either participate in the formation of secondary GHGs or greenhouse agents, or by affecting feedback parameters and hence alter the sensitivity of the Earth's climate system.

Emissions due to road vehicles come from the fuel cycle, vehicle production, vehicle operation and disposal as shown in figure 2. In this study we only look at the vehicle operation stage as the other stages are considered in other sectors such as the waste and industrial sectors.

## 2.1 Particulate Matter

Particulate matter (PM) is made up of solid and liquid particles suspended in air. It constitutes different elements with different sizes, radiative properties and health effects. Airborne PM has organic compounds and inorganic compounds, mainly sulphates, as main constituents, with some mineral dust, nitrates and black carbon (BC), often refered to as soot (Greenfacts, 2001-2007). However, in the case of road transport BC is the main constituent, especially in diesel vehicles (Kupiainen & Klimont, 2007).
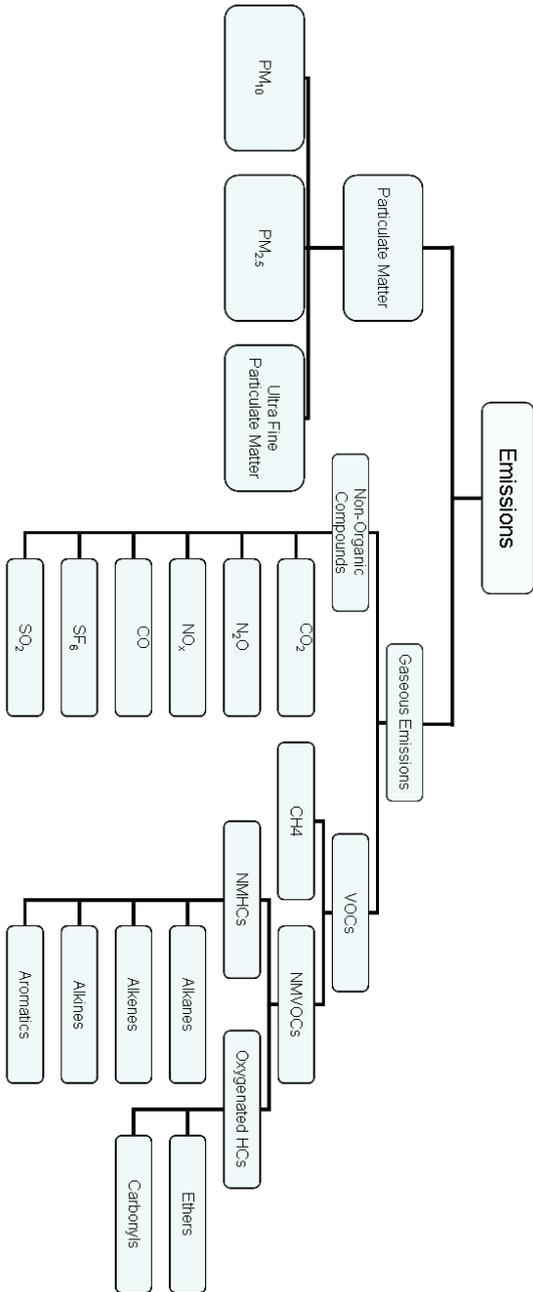
**Figure 1:** Classification of Anthropogenic Emissions
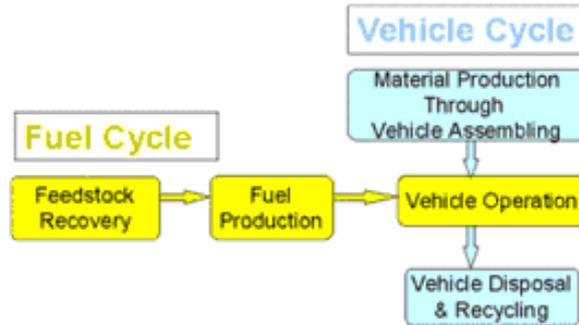
**Figure 2:** Vehicle life cycle assessment (Finnegan, n.d.)

PM is mainly classified by size as this governs transport and removal of the particles from the air, deposition into the respiratory system, and is associated with chemical composititon and source of the PM (Schwela & Zali, 1999). The main classes are $PM_{10}$ (course particles), $PM_{2.5}$ (fine particles) and $PM_{0.1}$ (ultrafine particles), where the subscript denotes the maximum aerodynamical diameter of the catergory and includes all smaller particles. Hence $PM_{10}$ is actually composed of course, fine and ultrafine particles.
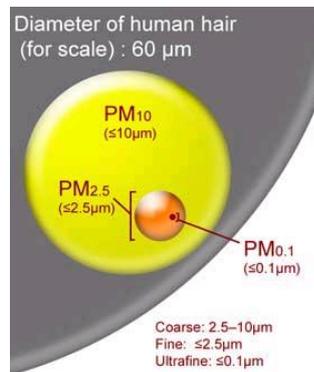


**Figure 3:** The size of particulate matter in relation to the diameter of human hair, which is taken to be 60 microns (Source: www.greenfacts.org/glossary/pqrs/PM10-PM2.5-PM0.1.htm)

The most observed PM is the mass of $PM_{10}$, with $PM_{2.5}$ (mainly in the range 0.1 to 2.5 $\mu$m) contributing 99% to this mass (Mazzi & Dowlatabadi, 2007). Larger particles tend to have short atmospheric lifetimes as they easily settle onto the ground, therefore do not accumulate. Smaller particles

(ultrafine) on the other hand have longer atmospheric lifetimes, and are the main contributor to PM numbers. However their mass density tends to be quite low hence have a very small contribution to the overall mass of airborne PM.

As a result of the significance of size to health and climate forcing $PM_{2.5}$ is gaining recognition by some councils and environmental agents (Laden, Neas, Dockery, & Schwartz, 2006). Particulates larger than $PM_{10}$ tend to be filtered out by the nose and throat, and if not are easily coughed out, thereby causing no health threat. $PM_{10}$, however, is inhaled with $PM_{2.5}$ penetrating deeper into lungs, reaching gas exchange regions. $PM_{0.1}$ passes through the lungs onto other organs, including the brain, hence have a greater health impact.

From a radiative perspective, most PM do not absorb radiation, but reflect and scatter it. This results in some of the radiation being reflected back into space, thereby reducing the net radiation at the top of the atmosphere (negative forcing). For the same mass of PM smaller particles will have a greater forcing. This is because they have a larger surface area with which to reflect and scatter radiation. Therefore fine particles, and more so ultrafine particles, are of significance to both climate and health.

PM can also be classified into primary and secondary PM, where primary PM is emitted as particulate and includes non-exhaust emissions such as break and tyre wear, road abrasions and dust raised by traffic induced turbulence. These tend to be larger particles, though we also have fine primary PM, e.g. BC. Seconday PM is as a result of gas-to-particle conversions and tends to be small. For example, sulphur dioxide ($SO_2$) is oxidised in into sulphuric acid ($H_2SO_4$), which in turn reacts with alkalines such as ammonia ($NH_3$) to form sulphates such as ammonium sulphate ($(NH_4)_2SO_4$). The same reactions occur for nitrogen dioxide, forming nitric acid ($HNO_3$) and nitrates
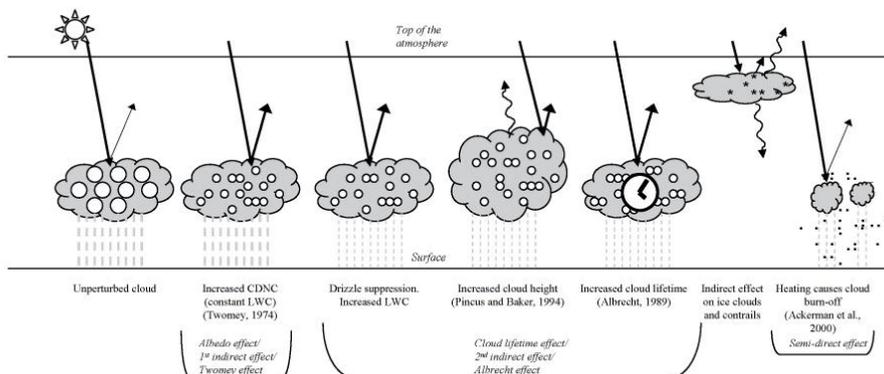
**Figure 4:** Schematic diagram showing the various radiative mechanisms associated with cloud effects that are significant for particulate matter. The black dots represent PM; the open white circles represent cloud droplets, indicating cloud droplet number concentration (CDNC); straight lines represent incident and reflected solar radiation; wavy lines represent terrestrial radiation; the vertical dashed lines represent rainfal; and LWC stands for liquid water content (Source: Foster & Ramaswamy, 2007)

such as ammoniun nitrate ($NH_4NO_3$).

PM also have indirect effects. They act as effective cloud condensation nuclei (CCN), thereby altering the earth's cloud cover and albedo. However, the cloud feedback effect is not yet well understood, making it difficult to quantify. This follows that despite knowing that increased CCN will result in increased cloud cover, we do not know the cloud type that will increase, and different cloud types have different feeedbacks.

**Black Carbon**

Some PM, mainly BC, is light absorbing. During incompete combustion, while most of the carbon is transformed into $CO_2$, CO and organic compounds (gaseous and particulate), a small fraction is emitted as black carbon. Compared to petrol combustion, diesel combustion tend to have a higher BC and is estimated to be 80-85% in the UK (Maynard & Howard, 1999). This forms part of the fine and ultrafine PM as it is mainly in the range 0.01 to 1 $\mu$m. BC is not measured, making it difficult to estimate its forcing and

climate impacts. However, the impacts of BC may be significant given that despite its short lifetime (less than a week) it has a high specific radiative forcing. Bond et al. (2004) suggested, based on a review of a study by Gillies and Gertler (2000), that BC constitute 66% of the $PM_{10}$ emitted by diesel engines, and 34% of that emitted by petrol engines, while in two stroke petrol engines it accounts for only 5% of the $PM_{10}$ emissions.

**PM trends**

Government policies mostly promote diesel vehicles. This is as a result of the lower $CO_2$ emissions from these vehicles and their higher energy efficiency. However, an increase in the diesel vehicle market share means an increase in PM emissions. This is further exacerbated by the rebound effect, which can be separated into vehicle-purchase rebound and travel rebound. With vehicle-purchase rebound, buyers switching to diesel vehicles tend to buy bigger cars, but this is becoming less the case as more small diesel vehicles are becoming available on the market. With the travel effect it has been observed that diesel vehicles tend to have a higher annual mileage compared to petrol vehicles. It is not well understood whether people drive long distances in diesel vehicles because the per-km cost is cheaper compared to petrol, due to higher fuel efficiency and lower diesel prices, or people buy diesel vehicles because of their need to travel long distances, which makes paying more for the vehicle purchase financialy sensible (Schipper et al., 2002).

However technologies are being put in place to cut down on PM emissions. These are in the form of particle traps. Mazzi and Dowlatabadi (2007) hypothesize that by 2009 all new diesel cars in Europe will have particle traps, and that by 2020 all diesel cars without particle traps will be scrapped off. However they also suggests that the particle traps may have 100% efficiency, but this is unlikely to happen as secondary particulate matter will still persist. On the other hand the German Federal Office for the Environment suggest

that particle traps may reduce ultrafine particle emissions from diesel vehicles by upto 95%.

## 2.2 Gaseous Emissions

Gaseous emissions consist of exhaust emissions and non-exhaust emissions, mainly evaporative loss emissions [1]. The grouping into direct GHGs, indirect GHGs and criteria pollutants can be useful, however some of the emissions, such as $CH_4$ and NMVOCs exhibit both direct and indirect forcing properties, while CO is a criteria pollutant but also exhibits indirect forcing. We will therefore not classify the emissions into these classes, but will say what forcing mechanism applies for each of the gaseous emissions.

### 2.2.1 Carbon Dioxide

Carbon dioxide, a long-lived greenhouse gas (LLGHG), has been an emission of major concern as far as radiative forcing and global change is concerned. As we shall see in section 3.2, $CO_2$ has a relatively low radiative efficiency. However, being a major emission during combustion processes, the high emission concentrations of $CO_2$ are a cause for concern.

It has also been noted that the introduction of measures to combat some of the emissions will actually lead to increased $CO_2$ emissions. For instance, while catalytic converters reduce the emissions of carbon monoxide (CO), volatile organic compounds and $NO_x$ (except for oxidising catalysts), they increase the emission of $CO_2$. Diesel particulate filters, on the otherhand, compromise the energy efficiency of the diesel engines, thereby increasing the diesel $CO_2$ emissions per kilometer. Fuel oxygenates are added to fuel

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[1]Evaporative loss emissions are emissions due to the evaporation and escape of volatile compounds from the fuel due to increased temperature during and shortly after engine run. They are often divided into diurnal, hot soak and running losses

in order to increase engine durability, lower fuel consumption, improve cold-starts, reduce exhaust emissions, etc. (Internatinal Programme on Chemical Safety, 1996). They achieve this by increasing the oxygen-fuel ratio, thereby reducing the emission of CO and VOCs, while offsetting $CO_2$ reductions due to the improving energy efficiency.

The emission trends for the UK since 1990 are shown in figure 5. The diesel
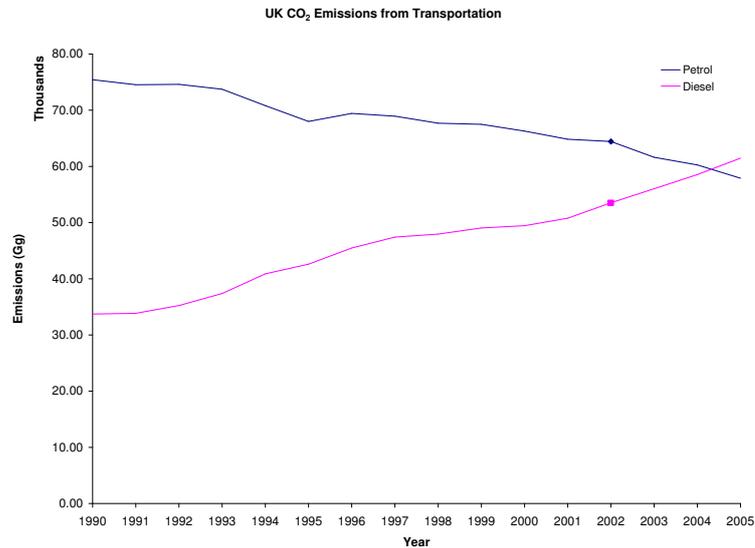


**Figure 5:** UK $CO_2$ emission trends from transportation, 1990-2005. Source:

emissions have been increasing over the period. In addition to the increase in $CO_2$ emissions resulting from the effect of emission reduction technologies there has been a further increase as a result of the increased diesel market share and vehicle km. Petrol engine efficiency has been improving. Were it not for the effect of the emission reduction technologies, $CO_2$ emissions by petrol vehicles would have been decreasing faster than they have.

### 2.2.2   Nitrous Oxide

Nitrous oxide ($N_2O$) is another LLGHG. Transportation is a significant contributor, with the UK recording a contribution of 14% in 2005. The emissions
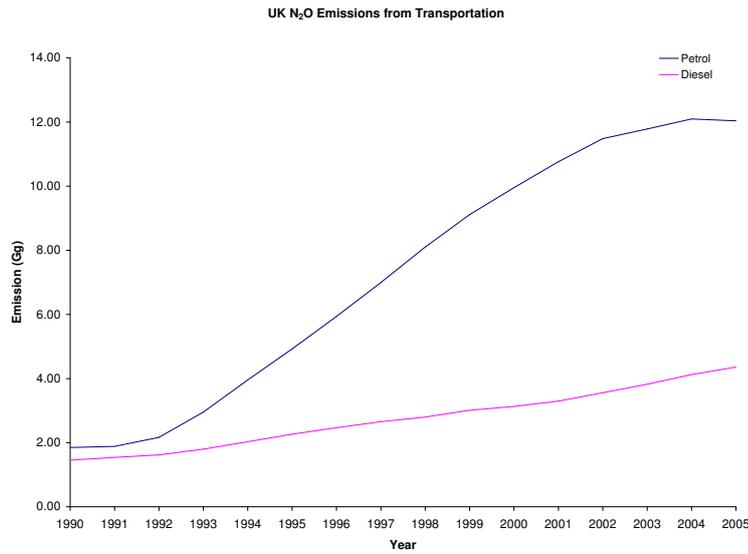


**Figure 6:**   UK $N_2O$ emission trends from transportation, 1990-2005. Source:

by both petrol and diesel vehicles have been increasing over the period running from 1990 to 2005 (figrue 6), with petrol emissions increasing at a faster rate. These increases correspond to increasing vehicle numbers and vehicle kilometers. The petrol emissions are further increased by the use of catalytic converters, which convert $NO_x$ into nitrogen and $N_2O$.

### 2.2.3   Methane

Methane ($CH_4$) is both a direct and indirect LLGHG. There are several contributions to the direct effects. These include the increase of tropospheric water vapour ($OH + CH_4 \rightarrow CH_3 + H_2O$) and ozone, which has the effect of reducing $CH_4$ levels and is included into the radiation efficiency of $1.3 \times$

$10^{-13}$ Wm$^{-2}$kg$^{-1}$. There is also the enhanced increase of CH$_4$ following CH$_4$ oxidation by OH. This results in an associated decrease of OH and hence a further increase in the CH$_4$ and accounts for a 33% increase on the radiative efficiency, hence the multiplication of the radiative efficiency by 1.3 (K. P. Shine et al., 2005). During the series of atmospheric reactions by CH$_4$ carbon dioxide is produced. However this effect is accounted for in the CO$_2$ radiative efficiency.

In the UK, the emissions have been decreasing as shown in figure 7. This
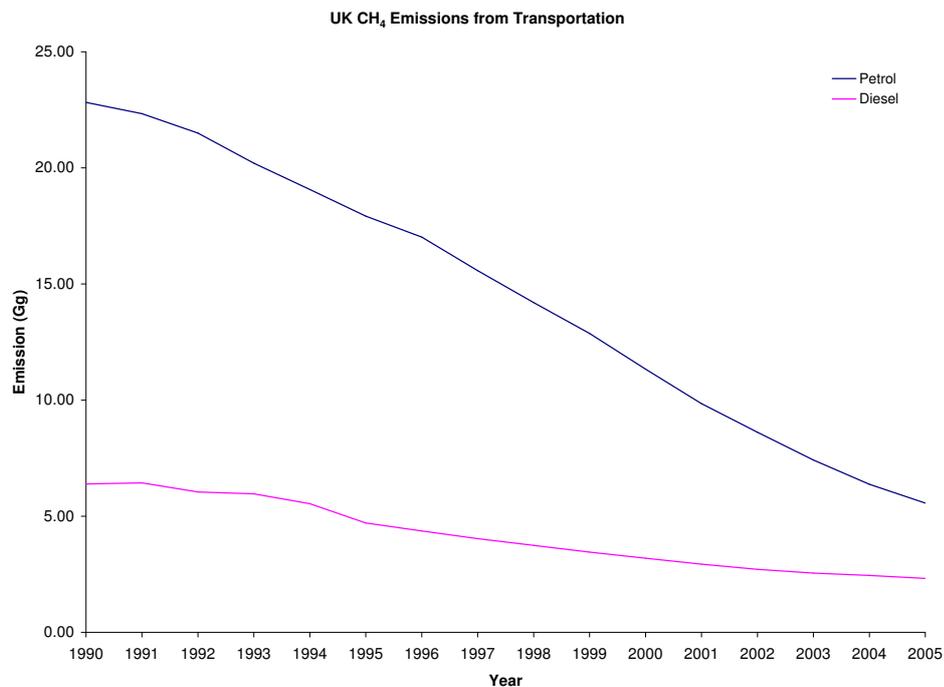


**Figure 7:** UK CH$_4$ emission trends from transportation, 1990-2005. Source:

is despite increasing vehicle kilometers and numbers, and is as a result of the use of catalytic converters. The increasing market share of the diesel vehicles slows down the reduction for diesel emissions, while petrol emissions are further reduced by the improving energy efficiency.

**2.2.4   Non-Methane Volatile Organic Compounds**

There are thousands of NMVOCs, which can be grouped into non-methane hydrocarbons (NMHCs) and oxygenates (ethers and carbonyls). A number of studies looking into the composition of road transport NMVOC have been conducted, e.g. Kristensson et al. (2004) and Schmitz et al. (2000), however, these do not give sufficient characterisation of the emissions.

Due to the lower energy efficiency of petrol cars compared to diesel cars, the per-km emissions of MNVOCs should be higher for petrol cars. However, not all road vehicle NMOC emissions are as a result of fuel combustion. Some are hot soak emissions (evaporative losses), which are higher at higher temperatures. Petrol tend to have higher evaporative losses due to its lower density, which is as a result of it consisting of lighter and therefore more volatile compounds. When the vehicles are idling, or moving downhill, the composition of evaporative NMOC emissions tends to be higher as the temperature is high enough to allow avaporation of VOCs and the combustion rate is low. In a tunnel study (Harley & Kean, 2004) it was found that the absolute NMOC emissions remained unchanged irrespective of whether the traffic flow was uphill or downhill. What changed was the composition, with more evaporative emissions during downhill drives.

The composition of the NMOC emissions is important since different compounds have different effects on environmental and human health. For example, polycyclic aromatic hydrocarbons (PAHs) are carcinogenic while benzene also increases susceptibility to leukaemia (Waverley Borough Council). It is dependant on fuel composition. However, there are no global standards for fuel. Different regions have different fuel chemical composition, which quite often also vary between different refiners within the same region. The geographical location also has an impact on the fuel composition. This is because in cold areas it can be difficult to ignite fuel. To counteract this more fuel

oxygenates such as ethanol and methyl tert-butyl ether (MTBE) are added into the fuel. However these tend to reduce the energy concentration of the fuel and increase the proportion of oxygenates in the emissions.

Staehelin et al. (1998) developed some emission factors for petrol and diesel NMHC emissions (table 2) using data collected from a tunnel in Switzerland with an average vehicle speed of 93 km h$^{-1}$. Despite having very high uncertainities (confidence intervals), this is the only study that gives information on the emission factors ($EF$) of NMHCs. The estimate of the emissions for a given year is given by

$$M_{NMHC} = EF \times \text{annual vehicle kilometers}$$

with the annual vehicle kilometers for 2002 reported by the Department for Transport (2003) to be $3.48 \times 10^{11}$ vehicle km for petrol and $1.38 \times 10^{11}$ vehicle km for diesel vehicles. This corresponds to 23 405 700 licenced petrol vehicles and 7 098 500 licenced diesel vehicles; that is $1.49 \times 10^{4}$ km per petrol vehicle and $1.94 \times 10^{4}$ km per diesel vehicle. This reflects the rebound effect and the fact that diesel vehicles have a high proportion of business vehicles, which tend to travel longer distances, e.g. public buses.

We only consider the NMHCs for which we have emission factors, lifetimes and specific radiation efficiency, which is ethane, propane, $n-$ and $i-$butane, $n-$pentane, $n-$hexane, $n-$heptane, ethene, $1-$butene, acetylene, benzene, toluene and $m+p$ xylene. Adding up these emissions for petrol and diesel we have $3.83 \times 10^{7}$ kg yr$^{-1}$ and $2.89 \times 10^{7}$ kg yr$^{-1}$ respectively. This corresponds to $1.1 \times 10^{-4}$ kg per vehicle km per year and $2.1 \times 10^{-4}$ kg per vehicle km per year. This is in contrary to the expectations generated by the above explainations. However, the accuracy of these emissions is in question given the unexplained high uncertainity of the emission factors (table 2).

These totals also do not agree with the total NMVOC totals reported by the Air Quality Expert Group (2007) for the same year, which are $1.72 \times 10^{8}$

| Group | NMHC | Radiative Forcing $(\mathrm{Wm}^{-2}\,\mathrm{ppbv}^{-1})$ [b] | $(\mathrm{Wm}^{-2}\,\mathrm{kg}^{-1})$ | Lifetime [a] (years) | Petrol EF | Diesel EF (mg per vehicle km) |
|---|---|---|---|---|---|---|
| Alkanes | Ethane | $3.2 \times 10^{-3}$ | $5.98 \times 10^{-13}$ | 0.0616 | $4.29 \pm 0.89$ | $3.21 \pm 4.51$ |
| | Propane | $3.1 \times 10^{-3}$ | $3.95 \times 10^{-13}$ | 0.0138 | $0.15 \pm 1.15$ | $5.73 \pm 5.85$ |
| | n-Butane | $4.7 \times 10^{-3}$ | $4.55 \times 10^{-13}$ | 0.0156 | $9.70 \pm 5.32$ | $27.25 \pm 27.05$ |
| | i-Butane | $4.7 \times 10^{-3}$ | $4.55 \times 10^{-13}$ | 0.0068 | $1.71 \pm 0.95$ | $5.18 \pm 4.84$ |
| | n-Pentane | $4.6 \times 10^{-3}$ | $3.59 \times 10^{-13}$ | 0.0040 | $6.16 \pm 4.45$ | $15.76 \pm 22.60$ |
| | n-Hexane | $4.7 \times 10^{-3}$ | $3.07 \times 10^{-13}$ | | $1.73 \pm 0.56$ | $2.85 \pm 3.10$ |
| | n-Heptane | $4.7 \times 10^{-3}$ | $2.96 \times 10^{-13}$ | | $0.93 \pm 0.44$ | $2.34 \pm 2.22$ |
| Alkenes | Ethene | $3.5 \times 10^{-2}$ | $7.02 \times 10^{-12}$ | 0.0019 | $24.14 \pm 6.12$ | $45.17 \pm 31.10$ |
| | 1-butene | $3.5 \times 10^{-2}$ | $3.51 \times 10^{-12}$ | | $1.92 \pm 0.61$ | $4.99 \pm 3.09$ |
| Alkynes | Acetylene | $3.3 \times 10^{-2}$ | $7.13 \times 10^{-12}$ | 0.0194 | $12.83 \pm 3.22$ | $15.84 \pm 16.36$ |
| Aromatics | Benzene | $3.4 \times 10^{-3}$ | $2.45 \times 10^{-13}$ | 0.0329 | $10.38 \pm 2.34$ | $15.41 \pm 11.90$ |
| | Toluene | $1.6 \times 10^{-2}$ | $9.76 \times 10^{-13}$ | 0.0066 | $20.43 \pm 6.89$ | $33.07 \pm 35.03$ |
| | m+p-Xylene | $2.4 \times 10^{-2}$ | $1.27 \times 10^{-12}$ | 0.0203 | $10.78 \pm 3.01$ | $27.17 \pm 15.29$ |
| | o-Xylene | $2.4 \times 10^{-2}$ | $1.27 \times 10^{-12}$ | | $4.77 \pm 0.56$ | $6.28 \pm 2.87$ |
| Carbonyls | formaldehyde | | | 0.0031 | $10.54 \pm 8.06$ | $67.75 \pm 36.45$ |
| | acetylehyde | | | 0.0013 | $2.33 \pm 1.12$ | $14.62 \pm 5.09$ |

**Table 2:** Some available constants for Non-Methane Organic Compounds

[a]Source: Seinfeld and Pandis (2006) for n-butane, benzene, toluene and $m+p$ xylene, otherwise Purvis et al. (2003)
[b]Source: Staehelin et al. (1998)

kg yr$^{-1}$ and $3.9 \times 10^7$ kg yr$^{-1}$ for petrol and disiel, respectively. The NMHC emission totals are acceptably lower than the NMVOC emissions as there are other NMHCs that have not been accounted for and other organic comounds (oxygenates). However, the total NMVOC emissions are in agreement with the theory.

### 2.2.5   Carbon Monoxide

Carbon monoxide (CO) is a pollutant of concern because if in high concentration it is rapidly absorbed in the lungs and passed onto the blood system where it reduces the amount of oxygen reaching organs and tissues, which can be fatal. CO is mainly a product of incomplete combustion and the main source is transportation, which accounts for more than two thirds of CO emissions in the USA (table 1) and almost 50% of the 2005 UK CO emissions.

CO is not only a threat to health but is also both a direct and indirect GHG. Like NMVOCs, it participates in the series of reactions that lead to the formation of ozone, which is both a GHG and a threat to environmental and human health.

The amount of CO emitted increases at low temperatures, and when the air-to-fuel ratio is low. This is often the case during acceleration, with engines that are not well tuned and at high altitudes where the air is thin, except in the case of vehicles that automatically adjust for altitude. The addition of fuel oxygenates however reduces CO emissions, so do catalytic converters and automatic adjustments for altitude.

CO is a weak direct GHG, and is therefore quite often not classified as a direct GHG. It however plays a significant role in the atmospheric levels of the hydroxyl free radical (OH), which in turn affects the levels of other

GHGs ($CH_4$ and ozone). This makes CO very significant in radiative forcing. It has been suggested (Wild & Prather, 2000; Derwent et al., 2001; Ehhalt & Prather, 2001) that CO has a specific radiative forcing that is 0.05 times that of $CH_4$ and the same adjustment time of 12 years.

### 2.2.6 Sulphur Dioxide

Sulphur dioxide is an irritant that can affect lung function if concentrations get up to 200 ppb (Waverley Borough Council). Most countries have air quality regulations covering $SO_2$. The emissions of $SO_2$ are expected to be dropping as a result of the introduction of sulphur low fuels. This is also necessiated by the use of emission controls as sulphur tend to be poisonous to both catalytic converters and particle traps.

Sulphur promotes nucleation (Palmgren et al., 2003), and is also oxidised to suphuric acid, which further react to form sulphates. All these process increase the amount of fine PM. Therefore a reduction in fuel sulphur content does not only reduce $SO_2$ emissions, but also reduces PM emissions and allows for the reduction of other emissions through allowing for the use of catalytic converters.

### 2.2.7 Oxides of Nitrogen

$NO_x$ constitute primarily of nitric oxide (NO) and nitrogen dioxide ($NO_2$), with more than 50% of anthropogenic $NO_x$ emissions being from transportation (table 1; Schwela and Zali (1999)). Diesel vehicles tend to have a higher $NO_2/NO$ ratio than petrol vehicles. NO on its own reacts with ozone, but

the series of reactions lead to no change in ozone concerntration:

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{2}$$

$$NO_2 + hv \rightarrow NO + O \tag{3}$$

$$O + O_2 \rightarrow O_3 \tag{4}$$

However, in the presence of hydrocarbons (including $CH_4$) and/or CO, a series of reactions converts NO into $NO_2$. In the presence of ultraviolet radiation $NO_2$ reacts with $O_2$ to form $O_3$. Therefore $NO_x$ have the effect of increasing $O_3$ concernatrations. Because of spatial and temporal dependence no global radiative efficiency has been prescribed for $NO_x$. However, Wild et al. (2001) estimated the radiative forcing for different regions. Their study revealed that $NO_x$ results in cooling, but this is after taking into consideration the $NO_x$–$CH_4$ effect which has already been accounted for in the $CH_4$ radiative efficiency. We will therefore consider the $NO_x$–$O_3$ radiative efficiency of $6.0 \times 10^{-13}$ $Wm^{-2}kg^{-1}$, noting that it is per kg of nitrogen, and a pertubation time 1.5 months, i.e. 0.125 years.

Like $SO_2$, $NO_x$ also reacts to form nitrates, contributing into the formation of secondary particulate matter. They also lead to the formation of acid rain, which cause environmental and economic damage. This happens as it changes the soil pH, hence affecting crop production and other living organisms in the soil, and causes material corrosion.

With the introduction of catalytic converters $NO_x$ emissions are expected to be dropping.

## 2.3  Summary of Emissions Comparison

The emissions from road transportation have been measured/estimated in different methods.

### 2.3.1  Data Collection Methods

**Dynamometer Measurements**

In this method the measurements are done by the dynamometer attached to the vehicle's exhaust system. This method is ideal for studying the effects of fuel additives, ambient temperature, drive-cycles, etc. on the emissions, but do not give a representation of the emissions for the entire fleet. This is compounded by the fact that the samples are usually small as the dynamometer cost limits the number of vehicles whos emissions can be measured. This becomes a source for some bias in the observations. Another source of this bias is the volunteers. Drivers of older vehicles and those who follow driving patterns that lead to higher emissions are unlikely to volunteer. Dynamometer measurements also target exhaust emissions, thereby do not include emissions due to evaporative losses (Harley & Kean, 2004). In this study we do not use any data collected through this method.

**Tunnel Measurements**

Road tunnels provide an atmosphere where the dilution of emissions is slow, therefore making it possible to collect air samples that are representative of the emissions. This method is ideal for studies aimed at the emissions for the entire fleet in a given area and time. However, it brings about the need to disaggregate the emissions. In this study we need data that is disaggregated into petrol and diesel vehicle emissions. In their study, Staehelin et al. (1998) used traffic counts, which were based on video counts run simultaneously to the emission sampling. These were used in the regression model to generate the disaggregated data for petrol and diesel vehicles.

**Estimations from Fuel Consumption**

With the exception of the emissions for NMHCs, emissions used in this study

are estimated using fuel consumption data and corresponding fuel emission factors. For example, the emission factor for methane is 21.24 kg/TJ and 13.91 kg/TJ of petrol and diesel, respectively (Biggott et al., 2007). This method is ideal as most countries will have fuel use statistics. However in some countries these statistics are not disaggregated into road transport and stationary machinary. In such cases the data is usually split up using estimated ratios. It is assumed these emission factors are a good average despite the different engine sizes, vehicle loads, driving patterns, etc.

### 2.3.2 Emissions Data for the UK, 2002

Ideally this project would compare global emissions from petrol and diesel vehicles. However, given the scarcity of dissaggregated data we only use the United Kingdom's emissions for the year 2002, summarised in table 3. In dealing with this data it is important to be aware of the high uncertainities in the individual NMOCs resulting from the uncertainities in emission factors shown in table 2. Almost 80% of the petrol VOC has not been accounted for, and 32% for diesel VOC. This is because some we have no emission factors for some NMVOC, while others have been left out because the lack of their radiative efficiencies and lifetimes means we can not analyse their effect any further. The NMVOCs that are accounted for may also have been under-estimated as a result of the emission efficiency uncertainities.

The $NO_x$, VOC and $PM_{10}$, and hence BC, emissions (Air Quality Expert Group, 2007) are based on fuel consumption, modelled by the NAEI emissions model.

$CO_2$ emissions (Biggott et al., 2007) are estimated from fuel consumption data using an emission factor of 855 kg of carbon per tonne of petrol and 863 kg of carbon per tonne of diesel. These emission factors are based on

| Pollutant | Petrol | Diesel | Source[a] |
|-----------|--------|--------|-----------|
| $CO_2$ | $6.44 \times 10^{10}$ | $5.35 \times 10^{10}$ | a |
| $N_2O$ | $1.15 \times 10^6$ | $3.56 \times 10^6$ | a |
| $NO_x$ | $2.85 \times 10^8$ | $4.26 \times 10^8$ | b |
| $CH_4$ | $8.61 \times 10^6$ | $2.72 \times 10^6$ | a |
| Ethane | $1.49 \times 10^6$ | $4.41 \times 10^5$ | c |
| Propane | $5.23 \times 10^4$ | $7.88 \times 10^5$ | c |
| n-butane | $3.38 \times 10^6$ | $3.75 \times 10^6$ | c |
| i-butane | $5.96 \times 10^5$ | $7.12 \times 10^5$ | c |
| n-pantane | $2.15 \times 10^6$ | $2.17 \times 10^6$ | c |
| ethene | $8.41 \times 10^6$ | $6.21 \times 10^6$ | c |
| Acetylene | $4.47 \times 10^6$ | $2.18 \times 10^6$ | c |
| Benzene | $3.62 \times 10^6$ | $2.12 \times 10^6$ | c |
| Toluene | $7.12 \times 10^6$ | $4.55 \times 10^6$ | c |
| m+p Xylene | $3.76 \times 10^6$ | $3.74 \times 10^6$ | c |
| other VOC | $3.55 \times 10^8$ | $2.67 \times 10^7$ | |
| **Total VOC** | $1.72 \times 10^8$ | $3.90 \times 10^7$ | b |
| BC | $8.84 \times 10^5$ | $1.78 \times 10^7$ | b* |
| **PM**$_{10}$ | $2.60 \times 10^6$ | $2.70 \times 10^7$ | b |

[a]The Sources are as follows:

a: The UK Greenhouse Gas Invetory, 1990 to 2005 (Biggott et al., 2007)

b: The Air Quality Expert Group (2007) publication

b*: The VOC emissions from the air-quality publication (b) is multiplied by 66% for diesel and 34% for petrol (Bond et al., 2004)

c: worked out using emission factors from Staehelin et al. (1998) and vehicle kilometers from Road Traffic Statistics: 2002 (Department for Transport, 2003)

**Table 3:** Emissions Comparison, emissions given in kg

the fuel carbon content and a set of equations (TRL equations) are used to separate the carbon to $CO_2$, CO and total hydrocarbon (THC) emissions.

$N_2O$ and $CH_4$ emissions (Biggott et al., 2007), on the otherhand, are estimated from measured emission factors (in g/km) and traffic statistics from the Department for Transport (DfT), a method similar to the one used for the NMHC emissions (section 2.2.4). These emission factors take into account the effects of different drive cycles (cold start emissions, hot exhaust emissions, vehicle speeds, etc.), different vehicle sizes/load, road type effects, and vehicle age and technology; which are all important factors contributing to emission factors.

We assumed that $PM_{10}$ constitutes of BC and sulphates. These are the main constituents, with nitrates and other constituants in smaller proportions. However, efforts to find radiative efficiency and avarage perturbation time for sulphates were not successful. Emissions data for CO dissaggregated into petrol and diesel could also not be solicited.

For both petrol and diesel $CO_2$ accounts for a large proportion of the emissions (about 99% by mass). A closer look at the non-$CO_2$ emissions reveals
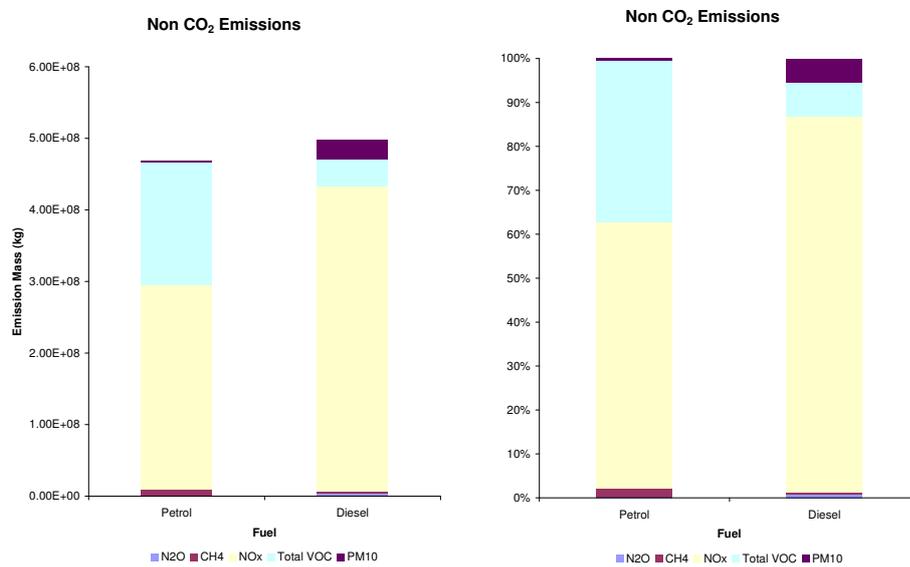


**Figure 8:** Non $CO_2$ emissions. the first chart shows the emission totals and the second shows the % contributions of the different constituents

that diesel cars emit a larger proportion of the non-$CO_2$ emissions, a large proportion of this being the nitrogen oxides, 86%, while they only constitute 61% of petrol non-$CO_2$ emissions. Petrol emissions however contribute 81% of the VOC emissions.

# 3   Metrics

As emissions from petrol and diesel fuel vehicles are 'climatically relevant' we need to consider the simple chain: emission changes → concentration changes → radiative forcing → climate impacts → societal and ecosystem impact → economic "damage". The relevance of impacts increase as we move down the chain, and so does uncertainity (K. P. Shine et al., 2005). Several metrics have been designed for this purpose. These go upto the 'climate impacts' level of the chain. Suggestions have been made for evaluating the damage using the Linear Damage Potential (LDP) and the Square Damage Potential (SDP) (K. Shine et al., 2005). These assume that the economic damage for a given area is either linearly or quadratically related to the climate impact. However, there are still a number of problematic issues with the damage and benefit metric (Foster & Ramaswamy, 2007), therefore will not be used herein.

In this section we consider three metrics based on the simplest climate model. These are the radiative forcing, global warming potential (GWP) and global temperature-change potential (GWT) (K. P. Shine et al., 2005). These metrics are global. Short-lived emissions do not last in the atmosphere long enough to be well mixed, and therefore are not only temporal but also spatially dependant. However, in the absence of metrics that are spatially dependant we shall employ these metrics for the short-lived emissions. (Foster & Ramaswamy, 2007)

## 3.1   Radiative Forcing

Radiative forcing, as defined by the IPCC, is an external perturbation in the radiative budget of the Earth's climate system. It is the change in net irradiance at the tropopause after allowing for stratospheric temperatures

to readjust to radiative equilibrium, while surface and tropospheric temperatures and state remain unperturbed (Ramaswamy et al., 2001). Vehicles are external to the climate system and their emissions create atmospheric concentration changes, and hence radiative forcing.

Radiative forcing is a function of the concentration of the forcing agent before and after the emission, with different expressions for different forcing agents. Simplified expressions for $CO_2$, $CH_4$, $N_2O$ and some CFCs are given by Ramaswamy et al. (2001), e.g.

$$\Delta F_{CO_2} = \alpha \left( g(C) - g(C_0) \right)$$

where $\alpha = 3.35$, C is the the concerntration of $CO_2$ emission in parts per million, $C_0$ is the initial concentration of $CO_2$ and

$$g(C) = ln \left( 1 + 1.2C + 0.005C^2 + 1.5 \times 10^{-6}C^3 \right)$$

However, if we assume that the emission concentrations remain sufficiently low, with linearisations about current concentrations, then the corresponding radiative forcing is independent of both the emission concentration and the concentration of other greenhouse gases (K. P. Shine et al., 2005). Radiative forcing constants for 1 kg emissions (also refered to as radiative efficiencies) of different greenhouse gases have been suggested. $N_2O$ and $CO_2$ radiative efficiencies have been updated in the resent IPCC fourth assessment report (Foster & Ramaswamy, 2007), hence different from those used by (K. P. Shine et al., 2005). The update includes all the constants used for the representation of $CO_2$ perturbation time. The efficiencies available in literature are presented in table 4, and table 5 for $CO_2$. This excludes the NMVOC radiative efficiencies already presented in table 2.

Radiative forcing can be estimated for instantaneous forcing, a single pulse emission or for continuous, sustained emissions. For instantaneous forcing we assume that all the forcing is at the time of the emission. For a 1 kg

| Emission | Radiative Forcing $(Wm^{-2}kg^{-1})$ | Perturbation time (years) |
|----------|--------------------------------------|---------------------------|
| $CH_4$   | $1.69 \times 10^{-13}$               | 12                        |
| $N_2O$   | $3.87 \times 10^{-13}$               | 144                       |
| $CO$     | $8.45 \times 10^{-15}$               | 12                        |
| $BC$     | $3.50 \times 10^{-9}$                | 0.015                     |

**Table 4:** Specific Radiation Efficiency and Response Time for Emissions. For NMHCs see table 2

| $i$      | 0       | 1       | 2       | 3     |
|----------|---------|---------|---------|-------|
| $a_i$    | 0.217   | 0.259   | 0.338   | 0.186 |
| $\alpha_i$ |       | 172.9   | 18.51   | 1.186 |
| $A_c$    | $1.79 \times 10^{-15}$ W m$^{-2}$kg$^{-1}$ | | | |

**Table 5:** Emission Parameters for $CO_2$. $\alpha_i$ is in years while $a_0$ is dimensionless

emission this forcing is equal to the radiative efficiency. To conduct a simple comparison of emissions from different sources, in our case petrol and diesel vehicles, we employ the following equation:

$$\Delta F_f = \sum_x \left( M_{f,x} \times A_x \right) \tag{5}$$

where $\Delta F_f$ is the total radiative forcing from source $f$, $M_{f,x}$ is the mass of emission $x$ emitted from source $f$ and $A_x$ is the specific (per unit mass) radiative forcing corresponding to emission $x$. In this (UK, 2002) case, the

|         | $A_x$ $(Wm^{-2} kg^{-1})$ | $\Delta M_{petrol,x}$ (kg) | $\Delta F_{petrol,x}$ $(Wm^{-2})$ | $\Delta M_{diesel,x}$ (kg) | $\Delta F_{diesel,x}$ $(Wm^{-2})$ |
|---------|---------------------------|----------------------------|-----------------------------------|----------------------------|-----------------------------------|
| $CO_2$  | $1.79 \times 10^{-15}$    | $6.44 \times 10^{10}$      | $115.2 \times 10^{-6}$            | $5.32 \times 10^{10}$      | $95.2 \times 10^{-6}$             |
| $CH_4$  | $1.69 \times 10^{-13}$    | $8.61 \times 10^{6}$       | $1.445 \times 10^{-6}$            | $2.72 \times 10^{6}$       | $0.459 \times 10^{-6}$            |
| $N_2O$  | $3.87 \times 10^{-13}$    | $1.15 \times 10^{7}$       | $4.451 \times 10^{-6}$            | $3.56 \times 10^{6}$       | $1.378 \times 10^{-6}$            |
| $NO_x{}^a$ | $6.00 \times 10^{-13}$ | $8.67 \times 10^{7}$       | $52.02 \times 10^{-6}$            | $1.30 \times 10^{8}$       | $78.0 \times 10^{-6}$             |
| $BC$    | $3.50 \times 10^{-9}$     | $8.84 \times 10^{5}$       | $3094 \times 10^{-6}$             | $1.78 \times 10^{7}$       | $62300 \times 10^{-6}$            |
| NMHCs$^b$ |                         | $3.50 \times 10^{7}$       | $107 \times 10^{-6}$              | $2.67 \times 10^{7}$       | $72.2 \times 10^{-6}$             |
| $\sum$  |                           | $6.4543 \times 10^{10}$    | $3.3781 \times 10^{-3}$           | $5.3381 \times 10^{10}$    | $6.2547 \times 10^{-2}$           |

$^a$The mass, $\Delta M$, is in kg of nitrogen.
$^b$This is a summation of the emission mass and forcings for ethane, propane, n-butane, i-butane, n-pentane, ethene, acetylene, benzene, toluene and m+p xylene. See table 2 for details

**Table 6:** Simple radiative forcing evaluated using equation 5

total radiative forcing is $\Delta F_{petrol} = 3.3781 \times 10^{-3}$ Wm$^{-2}$ and $\Delta F_{diesel} = 6.2547 \times 10^{-2}$ Wm$^{-2}$ for petrol and diesel vehicles, respectively. This reveals that diesel vehicles have a higher radiative forcing. This is as a result of having high BC emissions, which have a high specific radiative forcing and a short lifetime.

This is a good starting point for our comparison as it is simple and requires very few parameters. However it clearly does not consider the fact that the forcing occurs over the lifetime of the emissions, nor does it take into account the different lifetimes of the different emissions as shown in table 4. The forcing tends to decay exponentially with time, hence is expressed as

$$\Delta F = A_x R(t) \tag{6}$$

where $\Delta F$ is the radiative forcing at some time $t$ after the emission, $A_x$ is the radiation efficiency of the emission and $R(t)$ is the response function to the pulse emission, given by

$$R(t) = a_o + \sum_{i=1}^{3} a_i exp\left(\frac{-t}{\alpha_i}\right) \tag{7}$$

for $CO_2$, otherwise

$$R(t) = exp\left(\frac{-t}{\alpha}\right) \tag{8}$$

where $\alpha$ is the time constant for the removal of the gas from the atmosphere, sometimes refered to as the adjustment or perturbation time. This is not equivalent to the lifetime of the gas, but incooperates feedback effects (Ramaswamy et al., 2001; K. Shine et al., 2007).

For the NMHCs we assumed the perturbation times to be equal to the lifetimes given in table 2. These are taken from two sources, which are not consistent; the lifetimes from Purvis et al. (2003) being lower than those from Seinfeld and Pandis (2006). For example, according to Purvis et al. the lifetime of n-butane is 2.3 days while it is 5.7 days according to Seinfeld and

Pandis. In the case where the lifetime was given by both sources we use the lifetime by Seinfeld and Pandis. If indeed the lifetimes by Purvis et al. are an under estimate, then the radiative forcing estimated using them is also an under estimate.

The response function for $CO_2$ has a slightly more complex representation owing to the fact that its lifetime is determined by several uptake processes which have different uptake rates (Energy Information Centre, 2006). It is approximated by a "linear superposition of first order decay pools (equation (7)) with different time constants, $\alpha_i$ and fractional contributions, $a_i$" (Frolking et al., 2004), given in table 5. Though this linear superposition does not take into account some "nonlinearities in the carbon budget", it is still robust enough to be used (K. P. Shine et al., 2005).

In reality, most of the anthropogenic emissions, including road transport emissions, are sustained over time. We, therefore, define radiative forcing due to sustained emissions. In this case the radiative forcing is

$$\Delta F = A_x \Delta \chi(t) \tag{9}$$

where $\Delta \chi(t)$ is the concentration change and is given by

$$\Delta \chi(t) = \int_0^t \Delta S(t) R(t) dt \tag{10}$$

where $\Delta S$ is the emission change in kg yr$^{-1}$ (K. P. Shine et al., 2005). However, representing the emission change as a function of time is often not easy. This is especially the case with road transport emission, owing to the fact that there are many factors affecting the emissions which are difficult to model, e.g. driving cycles. Often the emission change is assumed to be constant over time, i.e. $\Delta S \neq \Delta S(t)$. We therefore have

$$\Delta \chi(t) = \alpha \Delta S \left[ 1 - exp\left( \frac{-t}{\alpha} \right) \right] \tag{11}$$

and in the case of $CO_2$ we have

$$\Delta\chi(t) = \Delta S \left\{ a_0 t + \sum_{i=1}^{3} a_i \alpha_i \left[ 1 - exp\left(\frac{-t}{\alpha_i}\right) \right] \right\} \qquad (12)$$

To evaluate the exponentially decaying radiative forcing we need to decide whether we would like to have the forcing at a given instant or the total forcing over a given time horizon. The latter gives more information on the impact of the emission and is defined as the global warming potential.

## 3.2 Global Warming Potential

The absolute global warming potential (AGWP) is the time integrated radiative forcing due to a 1 kg pulse emission,

$$AGWP = \int_0^t \Delta F dt \qquad (13)$$

The global warming potential (GWP) of a substance has been defined as the AGWP the substance relative to a reference gas. $CO_2$ has been used as the reference gas. Hence

$$GWP^x(t) = \frac{AGWP^x(t)}{AGWP^C(t)} \qquad (14)$$

The use of relative GWP is ideal for the comparison of the radiative forcing per kg of emission. This metric is widely used, especially in policy issues, including the Kyoto Protocol. The reason for this is that it is unequivocal and requires few input parameters. The Kyoto Protocol uses pulse radiation and a time period of 100 years, $GWP_{100}$. However, there is no restriction to the time horizon that can be used. In this work we evaluate the GWP for all the time horizons upto 500 years and pay particular attention to 20, 100 and 500 years, which are the time horizons consistently reported by the IPCC. We also define the GWP for sustained emissions ($GWP_s$) and then refer to the GWP due to a pulse emission as $GWP_p$. We also consider the absolute GWP as it gives us the exact impact of the emissions and can easily

be modified to give the impact of the actual emissions as opposed to the 1 kg used for the relative case.

### $GWP_p$

Substituting equation (6) together with the corresponding response function into (13) we have the absolute GWP for a 1 kg pulse emission,

$$AGWP_p^x = \frac{A_x}{C\left(\tau^{-1} - \alpha_x^{-1}\right)} \left[exp\left(-\frac{t}{\alpha_x}\right) - exp\left(-\frac{t}{\tau}\right)\right] \qquad (15)$$

and, in the case of $CO_2$,

$$
\begin{aligned}
AGWP_p^C &= \frac{A_C}{C} \left\{ \tau a_0 \left[1 - exp\left(-\frac{t}{\tau}\right)\right] \right. \\
&\left. + \sum_{i=1}^{3} \frac{a_i}{\tau^{-1} - \alpha_i^{-1}} \left[exp\left(-\frac{t}{\alpha_i}\right) - exp\left(-\frac{t}{\tau}\right)\right] \right\}
\end{aligned} \qquad (16)
$$

The different representation for $CO_2$ is as a result of $CO_2$ having a different response fuction.

Figure 9 shows the AGWP for a 1kg pulse emission evaluated for different time horizons. It increases until time horizon is equal to perturbation time, $\alpha$. Increasing the time horizon any further does not change the AGWP as the emission is completely removed from the atmosphere beyond $\alpha$. It is, therefore important to carefully select the time horizon based on the lifetimes of the emissions being studied if we want to compare their total global forcing. GWP on the otherhand does not increase with increasing time horizon as it is affected by the relativity to $CO_2$ radiative forcing. Instead it decreases as $CO_2$ has a longer perturbation time than all the other emissions under consideration. This means that the $CO_2$ forcing continues to increase long after the other emissions have been removed from the atmosphere.

We observe that of the three long-lived emissions $NO_2$ has the largest absolute GWP while $CO_2$ has the least. The short-lived emissions tend to have lower warming potentials, with the exception of BC, whose warming potential is actually higher than that of the long-lived emissions.
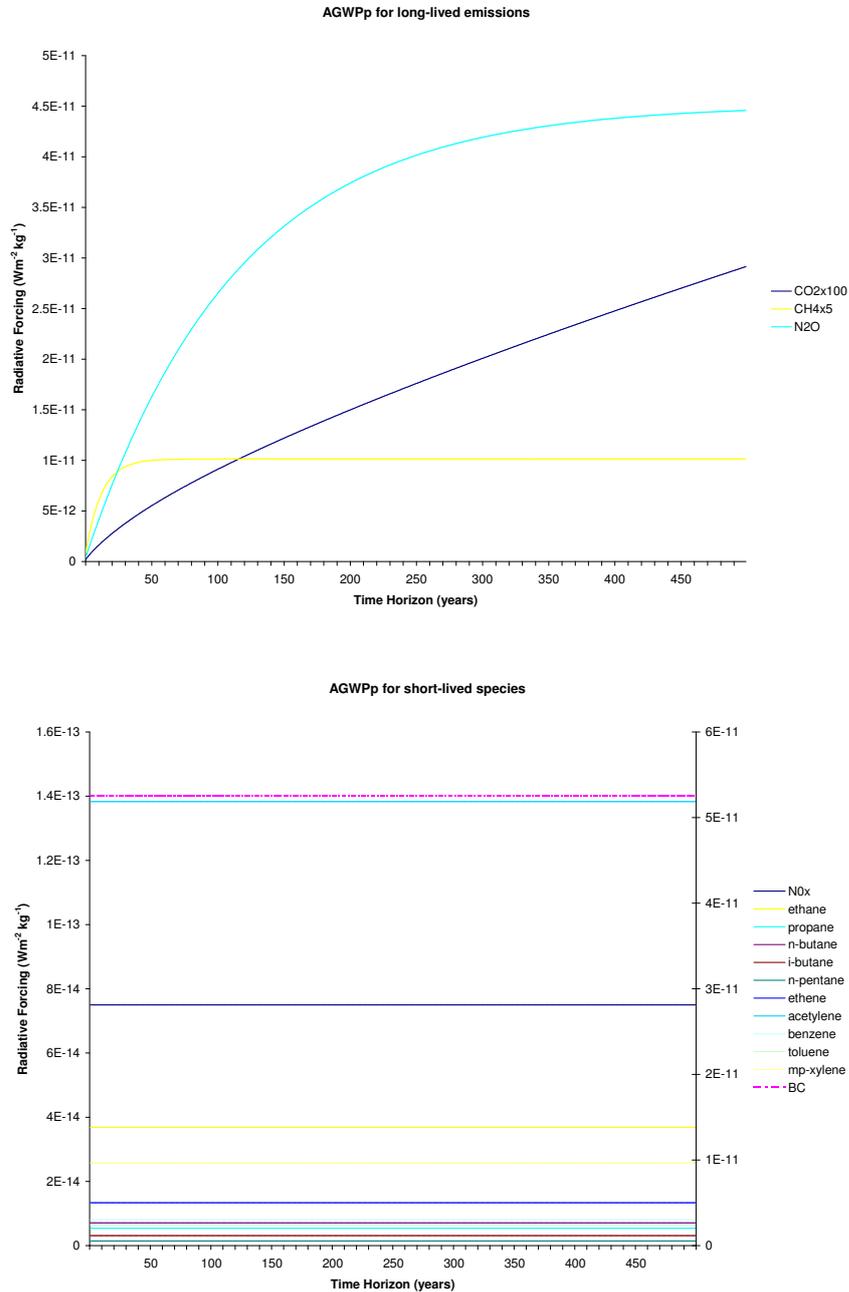
**Figure 9:** Absolute global warning potentials for a 1kg pulse emission. The emissions have been grouped into long-lived ($\alpha_x \geq 2$ years) and short-lived emissions. Black Carbon is plotted on the secondary axis of the second plot as its warming potential is much higher than the other short-lived emissions.
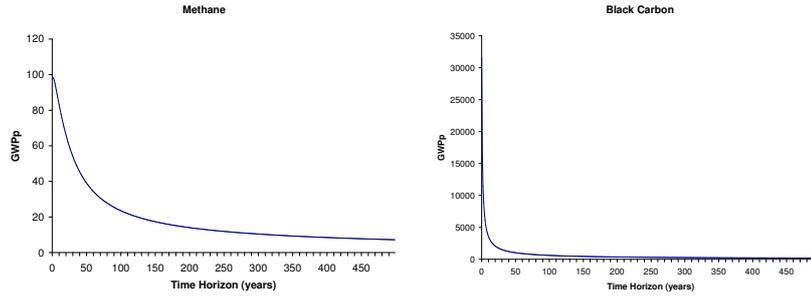
**Figure 10:** $GWP_p$ for methane and black carbon

**GWP$_s$**

Substituting equations (9) and the corresponding response function into equation (13) we have the absolute GWP for a sustained emission of 1 kg per year,

$$AGWP_s^x = A_x a_x \alpha_x \left[ t + \alpha_x \left( exp\left(\frac{-t}{\alpha_x}\right) - 1 \right) \right] \tag{17}$$

$$AGWP_s^C = A_c \left\{ \frac{1}{2} a_0 t^2 + \sum_{i=1}^{4} a_i \alpha_i \left[ t + \alpha_i \left( exp\left(\frac{-t}{\alpha_i}\right) - 1 \right) \right] \right\} \tag{18}$$

These should give us an indication of the global warming potential of sustaining the emissions thoughout the time horizon. For a 1 kg per year sustained emission of each gas we get the results shown on figure 11 and the GWPp for the 20, 100 and 500 years time horizon are presented in table 7.

|        | GWP$_s$ | | |
|--------|------|------|------|
|        | 20   | 100  | 500  |
| $CO_2$ | 1    | 1    | 1    |
| $CH_4$ | 68   | 24   | 7.2  |
| $N_2O$ | 292  | 301  | 155  |
| $NO_x$ | 3.08 | 0.88 | 0.27 |
| BC     | 2159 | 613  | 186  |

**Table 7:** Some of the GWP for time horizons 20, 100 and 500 years

In section 5 we consider the temperature change that would result from sustaining the 2002 road transportation emissions through out the time horizons considered.

**AGWPs for long-lived emissions**

**AGWPs for short-lived species**
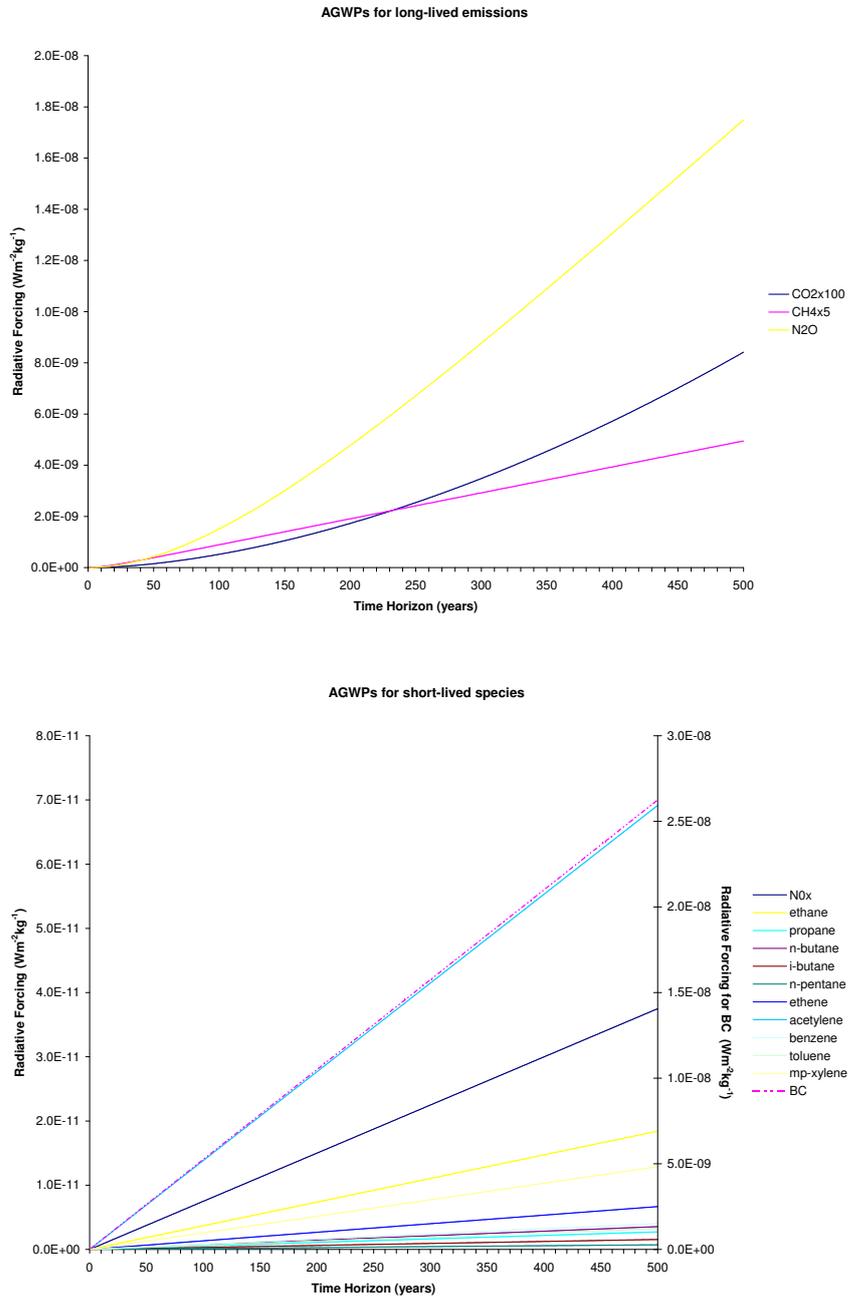
**Figure 11:** Absolute global warning potentials for a 1kg sustained emission. The emissions have been grouped into long-lived ($\alpha_x \geq 2$ years) and short-lived emissions. Black Carbon is plotted on the secondary axis of the second plot as its warming potential is much higher than the other short-lived emissions.

Comparing figure 11 to figure 9 we can see that the AGWPs is not limited by the perturbation time as the emission is continually being injected into the atmosphere. We also observe AGWP to increase linearly for short-live emissions.

## 3.3   Global Temperature Change Potential

We can go one step further down the chain onto climate impacts. One impact that is simple and unequivocal is the global temperature change which is simply represented by

$$C\frac{d\Delta T(t)}{dt} = \Delta F(t) - \frac{\Delta T(t)}{\lambda} \tag{19}$$

with the solution

$$\Delta T(t) = \frac{1}{C}\int_0^t \Delta F(t')exp\left(\frac{t'-t}{\tau}\right)dt' \tag{20}$$

where $C$ is the heat capacity of the system, $\lambda$ is the climate sensitivity and $\tau$ is the time constant of the system given by $\tau = C\lambda$.

We employ the Global Temperature Change Potential (GTP) as proposed by K. P. Shine et al. (2005), who argue that because of its simplicity and transparency this metric has the potential to supersede the GWP. Here we make the assumption that all the heat trapped by the Earth atmosphere is stored in the top 100 m of the oceans, which is the well-mixed layer. This assumption is based on the fact that the oceans cover about 71% of the Earth's surface and have a specific heat capacity which is approximately 4 times that of dry land. The heat capacity of the atmosphere is only comparable to that of the top 3.2 m of the ocean (Trenberth, 2005). Because it is well-mixed, we can assume that the top 100 m layer of the ocean is in thermal balance with the rest of the lower atmosphere. Therefore, in equation (19) and (20), $C$ is the heat capacity of the well-mixed layer of the ocean.

As expected, this metric will have more uncertainty than the GWP. This is due to the dependance on $\lambda$. This is inversely propotional climate feedbacks, some of which are still not well understood. We also assume $\lambda$ to constant. However this is not the case as emissions alter feedback effects and hence $\lambda$. Estimates of $\lambda$ range from 0.4 to 1.3 K (W m$^2$)$^{-1}$, which is an uncertainity of a factor of 3.

### 3.3.1 The Global Temperature Potential for Pulse Emissions

If we substitute equation (8) into (20) we can define the absolute global temperature change for a pulse emission to be

$$AGTP_p^x = \frac{A_x}{C\left(\tau^{-1} - \alpha_x^{-1}\right)} \left[\exp\left(\frac{t}{\alpha_x}\right) - \exp\left(\frac{t}{\tau}\right)\right], \tag{21}$$

assuming that $\alpha_x \neq \tau$. For CO$_2$ we substitute equation (7) into (20) and

$$
\begin{aligned}
AGTP_p^C &= \frac{A_C}{C} \left\{ \tau a_0 \left[1 - \exp\left(-\frac{t}{\tau}\right)\right] \right. \\
&\quad \left. + \sum_{i=1}^{3} \frac{a_i}{\left(\tau^{-1} - \alpha_i^{-1}\right)} \left[\exp\left(-\frac{t}{\alpha_i}\right) - \exp\left(-\frac{t}{\tau}\right)\right] \right\}
\end{aligned} \tag{22}
$$

This gives us information on how the temperature would change following a given pulse of emission. We observe that the temperature increases sharply during the lifetime of the emissions and then drops exponentially. The lifetime/perturbation time determines the time horizon at which we have maximum temperature change, whereas the radiative efficiency determines the magnitude of the maximum temperature change.

The temperature change due to CO$_2$ peaks at $7.77 \times 10^{-16}$ after 23 years. Unlike for the other emissions it does not drop to almost zero within the 500 years time horizon. This is as a result of the complexities due to the multiple removal procecces with different time constants. Minimizing CO$_2$ emissions, therefore, is a an effective way of minimizing temperature change in the long-run, whereas cutting down on shorter lived emissions with high radiative
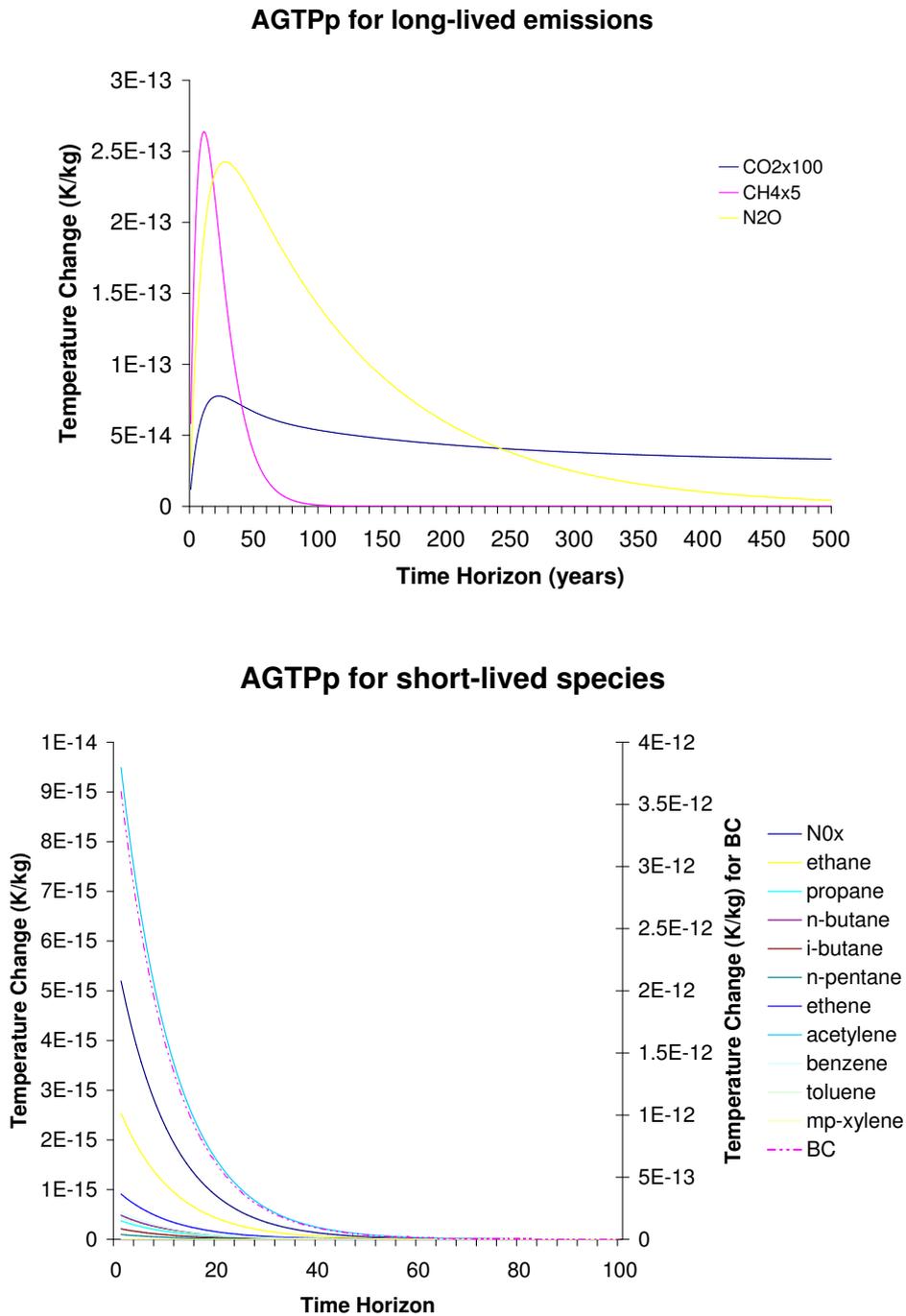
**Figure 12:** Absolute Global Temperature Potentials for a 1kg pulse of various emissions

efficiencies, such as BC, is effective in minimizing the maximum temperature change. The latter could be important in avoiding environmental damage that could result from the large temperature changes, even if they are short lived, and may help avoid abrupt climate change.
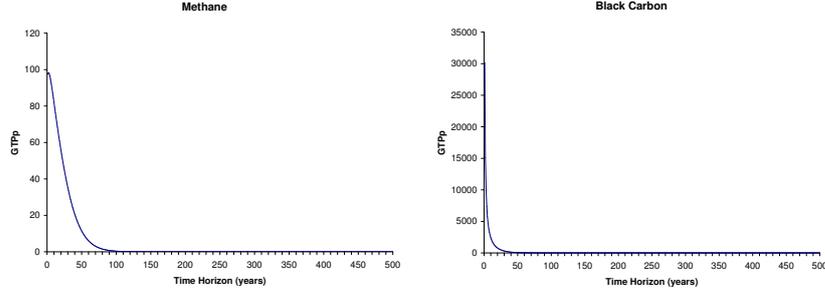


**Figure 13:** Global Temperature Potentials for a 1kg pulse of methane (long-lived) and black carbon (short lived)

### 3.3.2   The Global Temperature Potential for Sustained, Constant Emissions

For sustained emissions, constant at 1 kg yr$^{-1}$, we substitute equation (9) and (10) into (20), which gives us

$$
\begin{aligned}
AGTP_s^x(t) \;=\; & \frac{\alpha_x A_x}{C} \left\{ \tau \left[ 1 - \exp\left( -\frac{t}{\tau} \right) \right] \right. \\
& \left. - \frac{1}{\tau^{-1} - \alpha_x^{-1}} \left[ \exp\left( -\frac{t}{\alpha_x} \right) - \exp\left( -\frac{t}{\tau_x} \right) \right] \right\}
\end{aligned}
\tag{23}
$$

For $CO_2$ we have

$$
\begin{aligned}
AGTP_s^C(t) \;=\; & \frac{A_C}{C} \left\{ a_o t \tau - a_o \tau^2 \left[ 1 - \exp\left( -\frac{t}{\tau} \right) \right] \right. \\
& + \sum_{i=1}^{3} \alpha_i a_i \left[ \tau \left( 1 - exp\left( -\frac{t}{\tau} \right) \right) \right. \\
& \left. \left. - \frac{1}{\tau^{-1} - \alpha_i^{-1}} \left( exp\left( -\frac{t}{\alpha_i} \right) - exp\left( -\frac{t}{\tau} \right) \right) \right] \right\}
\end{aligned}
\tag{24}
$$

The temperature change due to sustained emissions increases with time. This continues while until the rate at which the emission is being injected into the atmosphere balances with the rate of removal. Longer lived emissions

take longer to reach this balance. If the emission rate, $\Delta S$, increased (decreases) after this balance has been achieved, the temperature change will also increase (decrease) until a new balance is achieved. This implies that if measures to reduce anthropogenic emissions, in particular from road transportation are put in place, the temperature change can gradually be reduced. However, we need to sufficiently reduce anthropogenic emissions "to avoid dangerous interference with the climate system" (UNFCCC, 1992) with the European Union suggesting no more than a temperature change of 2K between the pre-industrial and 2100 global average temperature (Subak et al., 1997).
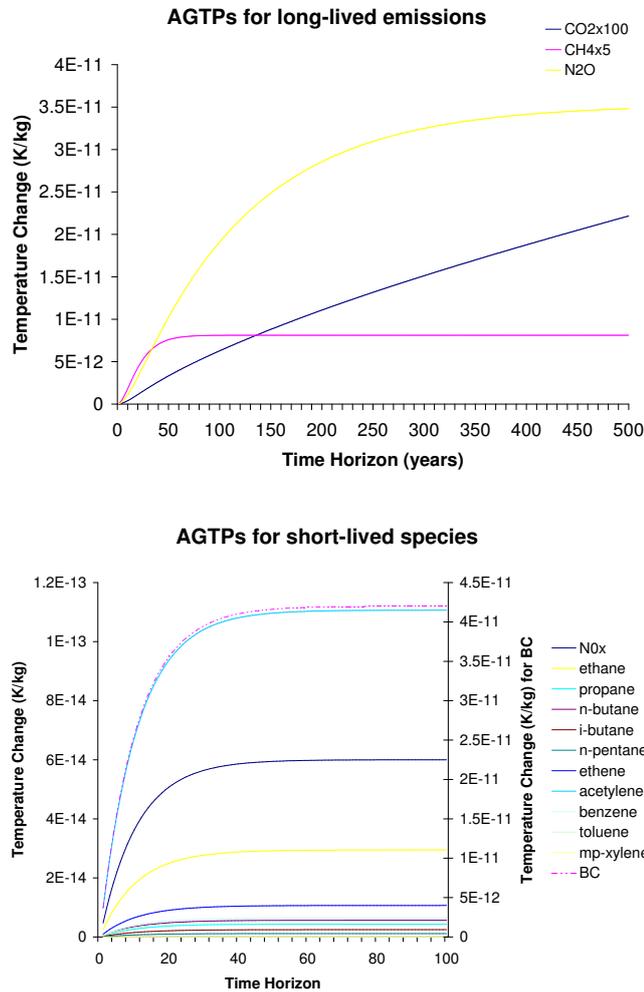
**Figure 14:** Absolute Global Temperature Potentials for a 1kg/yr sustained emission of various emissions
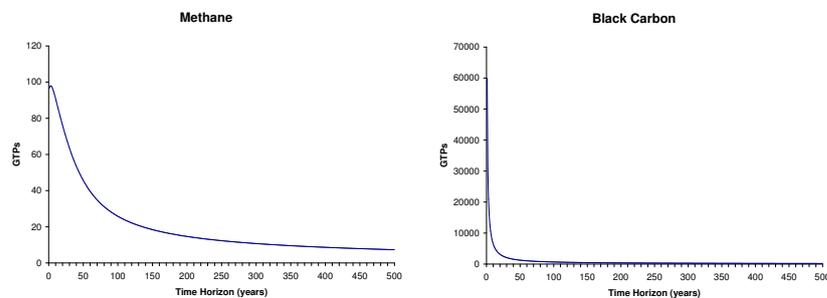


**Figure 15:** Global Temperature Potentials for a 1kg/year sustained emission of methane (long-lived) and black carbon (short lived)

# 4   Deep Ocean Global Temperature Change Potential

Not all of the radiation energy that comes into the Earth atmosphere system is stored in the ocean mixed layer. Despite the existence of the thermo-
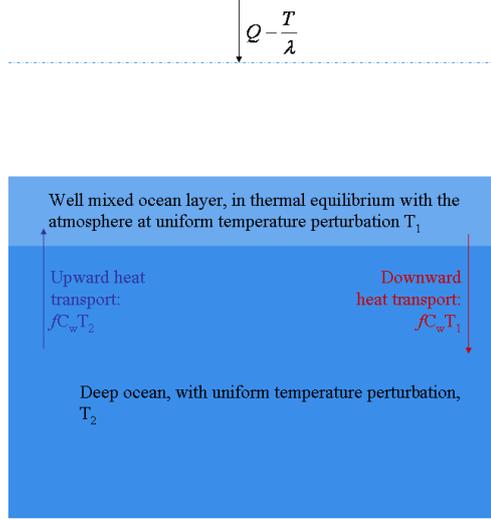


**Figure 16:** Schematic of the Deep Ocean Model, showing simplified energy transfer between the well mixed layer and the deep ocean

cline, upwelling, downwelling, convective overturning and downward diffusion transport energy between the mixed layer and the deep ocean (Harvey, 2000). This means that some thermal energy is transfered to the deep ocean, and therefore the maximum temperature change should be lower than that given by the GTP. However, the impact of the emissions should be spread over a longer time period as the deep ocean serves as a memory for the climate system. We consider the simplified zero dimensional model given by the following system of equations:

$$C_1 \frac{\partial T_1(t)}{\partial t} = \Delta F - \frac{T_1}{\lambda} - fc_w (T_1 - T_2) \qquad (25)$$

$$C_2 \frac{\partial T_2(t)}{\partial t} = fc_w (T_1 - T_2) \qquad (26)$$

where the subscript 1 represents the mixed layer while 2 represents the deep ocean and $T_x$ $(x = 1, 2)$ is actually the temperature change in the repective

layer. As before, the atmosphere is in thermal balance with the mixed layer. This model assumes that the temperature in the deep ocean only changes as a result of heat transfer from the mixed layer. For simplicity all the processes that transport energy between the two layers are grouped and represented by $fc_w(T_1 - T_2)$, where $c_w$ is the specific heat of water at standard temperature and pressure $(4.18 \times 10^3 \text{ J kg}^{-1} \text{ K}^{-1})$. $f$ is the water mass flux between the two layers, assumed to be constant with time and estimated to be $f = 1.76 \times 10^{-4}$ kg m$^{-2}$ s$^{-1}$ (derived using the flux estimate of $2 \times 10^{15}$ m$^3$ yr$^{-1}$ (Jacob, 1999) and the 71% coverage of the Earth surface by oceans).

Differentiating (25) with respect to time gives a second order differential

$$\frac{\partial^2 T_1(t)}{\partial t^2} + A_1 \frac{\partial T_1(t)}{\partial t} + A_2 T_1(t) = A_3 \tag{27}$$

where

$$A_1 = \beta_1 + \beta_2 + \tau^{-1}$$
$$A_2 = \beta_2 \tau^{-1}$$
$$A_3 = \frac{1}{C_1} \frac{\partial(\Delta F)}{\partial t} + \frac{\beta_2 \Delta F}{C_1}$$

and

$$\beta_1 = \frac{fc_w}{C_1},$$
$$\beta_2 = \frac{fc_w}{C_2}, \quad \text{and}$$
$$\tau = C_1 \lambda.$$

where $C_1$, the heat capacity of the well-mixed layer, is $4.2 \times 10^8$ JK$^{-1}$m$^{-2}$ and $C_2$, the heat capacity of the deep ocean, is assumed to be 30 times $C_1$ $(1.26 \times 10^{10}$ JK$^{-1}$m$^{-2})$. We note that

$$A_1^2 - 4A_2 = \beta_1^2 + \beta_2^2 + \tau^{-2} + 2\beta_1\beta_2 + 58\beta_2\tau^{-1} > 0$$

and therefore the homogeneous equation has a solution of the form

$$T_1(t) = k_1 e^{r_1 t} + k_2 e^{r_2 t}$$

with

$$r_1 = 0.5 \left( -A_1 + \sqrt{A_1^2 - 4A_2} \right)$$

$$r_2 = 0.5 \left( -A_1 - \sqrt{A_1^2 - 4A_2} \right)$$

We consider the following radiative forcing:

1. instantaneous (or constant) forcing

2. pulse forcing

3. constant sustained forcing

and solve for the particular solution. These are initial value problems. At the time of the emission, $t = 0$, the temperature change for both the mixed layer and the deep ocean layer is zero, i.e.

$$T_1 = T_2 = 0$$

Substituting this into equation (25) we have

$$\frac{\partial T_1}{\partial t} \bigg|_{t=0} = \frac{\Delta F}{C_1}$$

## 4.1   Instantaneous Forcing

If we assume the forcing due to an emission all occurs at one instant and solve the IVP, we have

$$\Delta F = A_x \tag{28}$$

and the temperature change is given by

$$T_1(t) = k_1 e^{r_1 t} + k_2 e^{r_2 t} + k_3 \tag{29}$$

where $k_3$ is derived from the particular solution while $k_1$ and $k_2$ are derived from the initial conditions, and

$$k_3 = \frac{A_3}{A_2} = \frac{A_x}{A_2} = A_x k_3'$$

$$k_1 = \frac{A_x}{r_1 - r_2}\left(\frac{1}{C_1} + \frac{r_2}{A_2}\right) = A_x k_1'$$

$$k_2 = \frac{A_x}{r_2 - r_1}\left(\frac{1}{C_1} + \frac{r_1}{A_2}\right) = A_x k_2'$$

**Methane**



**Black Carbon**
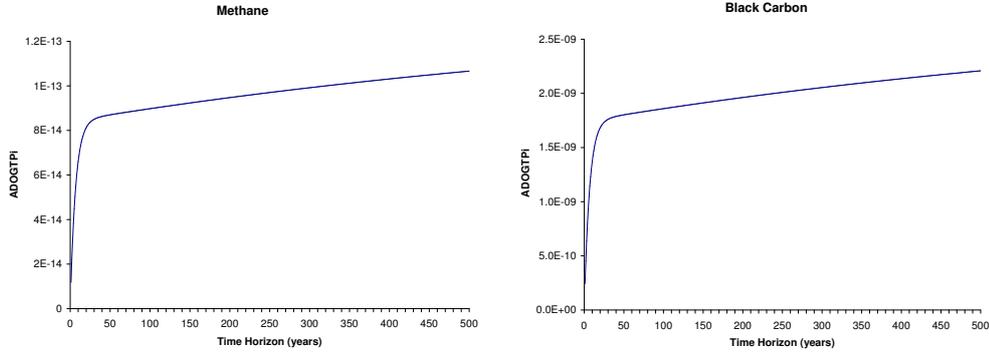


**Figure 17:** Temperature change due to constant forcing in K kg$^{-1}$ for a long-lived (CH$_4$) and a short-lived (BC) emission

Figure 17 shows that following an instantaneous forcing the temperature will change at a fast rate over the first 25 years, irrespective of the perturbation time. However this model does not account for the removal of the emissions from the atmosphere, hence the temperature change does not drop despite the system's release of the energy through thermal radiation.

## 4.2 Pulse Emission Forcing

Here we consider forcing that decays exponentially with time (equation (8)). This gives a temperature change of

$$T_1(t) = k_1 e^{r_1 t} + k_2 e^{r_2 t} + k_3 e^{-t/\alpha_x} \tag{30}$$

By the particular solution

$$k_3 = \frac{A_x \alpha_x}{C_1} \frac{\beta_2 \alpha_x - 1}{A_2 \alpha_x^2 - A_1 \alpha_x + 1} = A_x k_3'$$

and by the initial conditions

$$k_1 = \frac{A_x k_3'(\alpha_x^{-1} + r_2) + \frac{A_x}{C_1}}{r_1 - r_2} = A_x k_1'$$

$$k_2 = \frac{A_x k_3'(\alpha_x^{-1} + r_1) + \frac{A_x}{C_1}}{r_2 - r_1} = A_x k_2'$$

For $CO_2$ the temperature change is

$$T_1(t) = k_1 e^{r_1 t} + k_2 e^{r_2 t} + k_3 e^{-t/\alpha_x} + \sum_{i=1}^{3} k_{3+i} \exp\left(-\frac{t}{\alpha_i}\right) \qquad (31)$$

with the particular solution yielding

$$k_3 = \frac{A_c \beta_2 a_o}{A_2 C_1} = A_c k_3'$$

$$k_{3+i} = \frac{A_c \alpha_i}{C_1} \frac{\beta_2 \alpha_1 - a_i}{A_2 \alpha_i^2 - A_1 \alpha_i + 1}, \qquad i = 1, \dots, 3 = A_c k_{3+i}'$$

and, by the initial conditions,

$$k_1 = \frac{1}{r_1 - r_2} \left\{ A_c k_3' r_2 + \frac{A_c a_0}{C_1} + \sum_{i=1}^{3} \left[ \left(r_2 + \alpha_i^{-1}\right) k_{3+i} + \frac{A_c a_i}{C_1} \right] \right\} = A_c k_1'$$

$$k_2 = \frac{1}{r_2 - r_1} \left\{ A_c k_3' r_1 + \frac{A_c a_0}{C_1} + \sum_{i=1}^{3} \left[ \left(r_1 + \alpha_i^{-1}\right) k_{3+i} + \frac{A_c a_i}{C_1} \right] \right\} = A_c k_2'$$

Figure 18 shows a comparison of the global temperature potential as modelled by the simplest model to that by the deep ocean model. The latter has a lower maximum temperature change, and the temperature change approaches zero at a slower rate. This is because initially some heat is transfered to the deep ocean, hence the lower temperature change.

The difference between the maximum temperature change predicted by the two models is a function of the perturbation time, with a longer perturbation time having a larger temperature difference. This is because if the
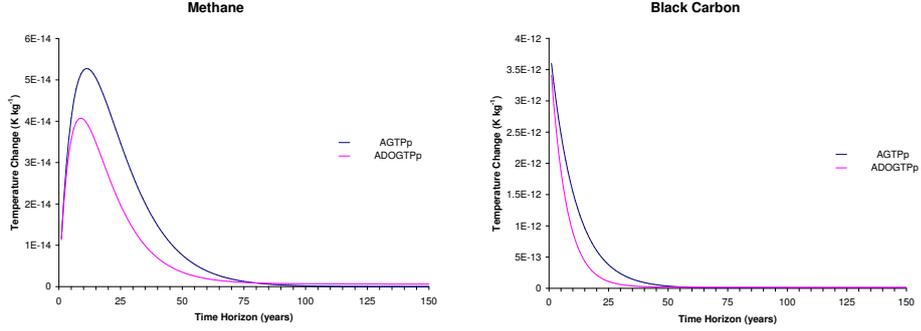
**Figure 18:** Global Temperature Potentials for a 1kg pulse of methane (long-lived) and black carbon (short lived)(Deep ocean model)

perturbation time is short the rate of temperature change is high, giving the system little time to transfer heat to the deep ocean.

As the emission is being removed from the atmosphere the atmospheric temperature change begins to drop. The rate at which it drops will however be slowed down by the fact that the upwelling ocean waters are warmer than they were initially as a result of the heat that has been stored in the deep ocean.

## 4.3   Constant Sustained Forcing

$$T_1(t) = k_1 e^{r_1 t} + k_2 e^{r_2 t} + k_3 e^{-t/\alpha_x} + k_4 \tag{32}$$

where

$$
\begin{aligned}
k_3 &= \frac{A_x \alpha_x^2}{C_1} \frac{1 - \beta_2 \alpha_x}{A_2 \alpha_x^2 - A_1 \alpha_x + 1} = A_x k_3' \\
k_4 &= \frac{A_x \beta_2 \alpha_x}{A_2 C_1} = A_x k_4'
\end{aligned}
$$

(particular solution) and

$$
\begin{aligned}
k_1 &= \frac{A_x k_3' \left( r_2 + \alpha_x^{-1} \right) + A_x k_4' r_2}{r_1 - r_2} = A_x k_1' \\
k_2 &= \frac{A_x k_3' \left( r_1 + \alpha_x^{-1} \right) + A_x k_4' r_1}{r_2 - r_1} = A_x k_2'
\end{aligned}
$$

46

(initial conditions) with $A_1$ and $A_2$ as before.

For $CO_2$ we have

$$T_1(t) = k_1 e^{r_1 t} + k_2 e^{r_2 t} + k_3 + \sum_{i=1}^{3} k_{3+i} \exp\left(-\frac{t}{\alpha_i}\right) \qquad (33)$$

where the particular solution gives us

$$
\begin{aligned}
k_3 &= \frac{A_x}{A_2 C_1}\left[a_0\left(1 + \beta_2 t\right) + \beta_2 \sum_{i=1}^{3} a_i \alpha_i\right] = A_x k_3' \\
k_{3+i} &= \frac{A_x a_i \alpha_i^2}{C_1}\frac{1 - \beta_2 \alpha_i}{A_2 \alpha_i^2 - A_1 \alpha_i + 1} = A_x k_{3+i}', \qquad i = 1,\ldots,3
\end{aligned}
$$

and by the initial conditions

$$
\begin{aligned}
k_1 &= \frac{A_x}{r_1 - r_2}\left[k_3' r_2 + \sum_{i=1}^{3}\left(r_2 - \alpha_i^{-1}\right) k_{3+i}'\right] = A_x k_1' \\
k_2 &= \frac{A_x}{r_2 - r_1}\left[k_3' r_1 + \sum_{i=1}^{3}\left(r_1 - \alpha_i^{-1}\right) k_{3+i}'\right] = A_x k_2'
\end{aligned}
$$

We observe that for the simple model the rate of accumulation of the emis-
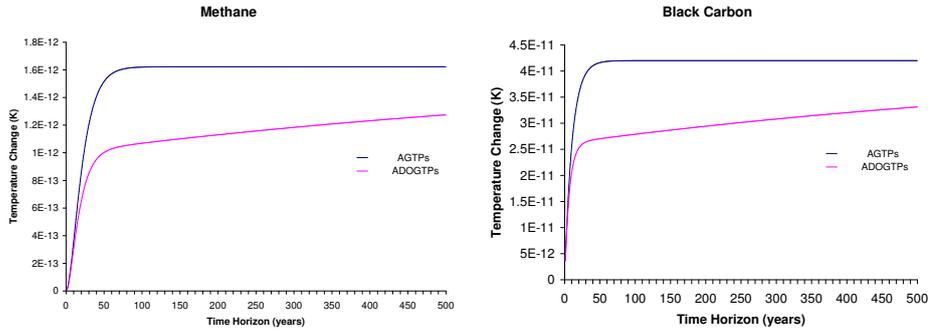


**Figure 19:** Global Temperature Potentials for a 1kg/yr sustained emission of methane (long-lived) and black carbon (short lived)(Deep ocean model)

sion balances the removal rate the temperature change stabilises. However, according to the deep ocean model the temperature change continues to increase at a slower rate. This happens as the deep ocean becomes warmer with time and therefore recieves energy at a decreasing rate.

**A Note on Deep Ocean GTP for $CO_2$**

As a result of the different radiative forcing representation for $CO_2$ we had to derive separate equations for the temperature change forced by $CO_2$ (equations (31)and (33). These mathematical models yielded the results shown in figure 20. These results do not represent what is expected to happen following $CO_2$ emissions. When we considered a pulse emission of 1 kg the model
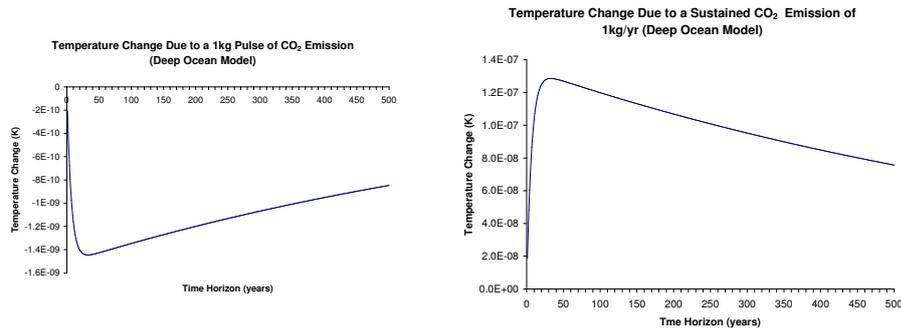


**Figure 20:** Deep ocean model for $CO_2$: not fitting physical atmospheric behaviour

results show some cooling, yet $CO_2$ should have a positive radiative forcing, and therefore result in a temperature increase. For the sustained emission the modelled temperature change is about 6 orders of magnitude higher than what we have from GTPs. This contradicts theory as we would expect to have the same order of magnitude, with the deep ocean model initially giving lower temperature changes.

This represents an error in the model. However, within the constraints of time we could not identify whether the error is in the mathamatical derivation or in the model coding. We therefore do not use the deep ocean model for $CO_2$.

# 5   Petrol-Diesel Emissions Comparison

In conducting this comparison we use the metrics discussed in the preceding sections. Instead of using a 1kg emission we use the 2002 vehicle emissions for the UK, hence we multiply the radiative efficiency, $A_x$ by the emission mass. Since all our metrics are multiples of $A_x$, multiplying through by the mass gives the impact of the emission.

We begin by looking at the emissions due to the total fleet of conventional fuel vehicles, and then proceed to consider the per vehicle kilometer emission.

## 5.1   Emissions From All Conventional Vehicles

### 5.1.1   Total Emissions and $CO_2$ Emissions

We assume that both the radiative forcing and temperature change by the emission constituents are accumulative and therefore can add them up to evaluate the total impact. This gives the results shown in figure 21.

Comparing the total impact to the impact due to $CO_2$ (figure 22) we find that most of the impact is as a result of the forcing due to $CO_2$. This implies that to minimize the impact of vehicles on climate we need to cut down on $CO_2$ emissions as much as possible, hence the importance of developing more energy efficient engines.

### 5.1.2   Non-$CO_2$ Emissions

In the light of their impacts on both the climate system and environmental health, we can not ignore the non-$CO_2$ constituents of the emissions. Figure 23 shows the contributions to temperature change for a scenario where the 2002 emissions are sustained. The non-$CO_2$ emissions from diesel vehicles
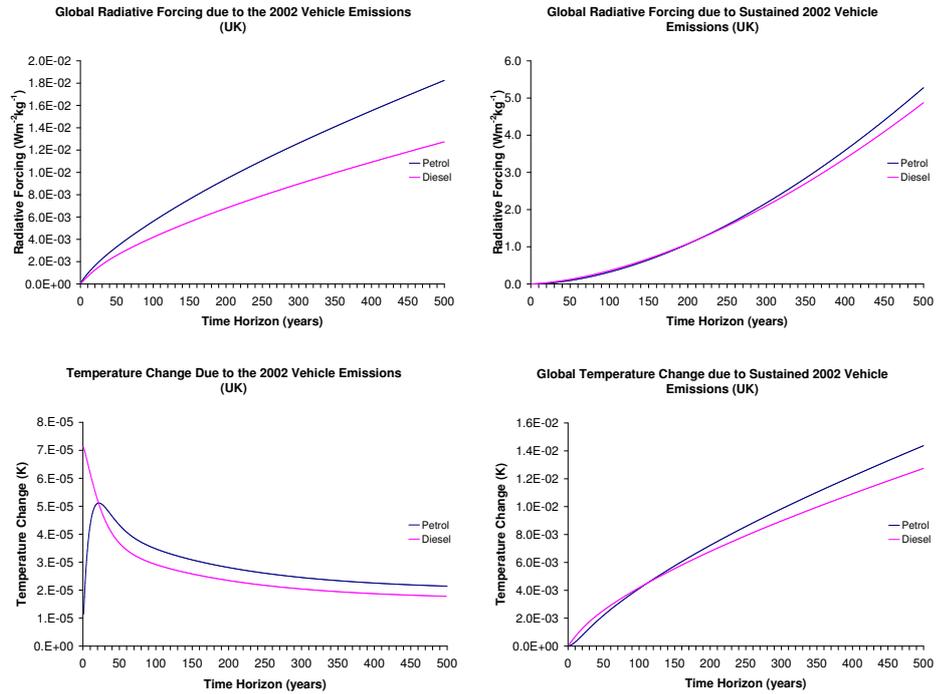
**Figure 21:** Comparison of the impact of total emissions from petrol and diesel vehicles
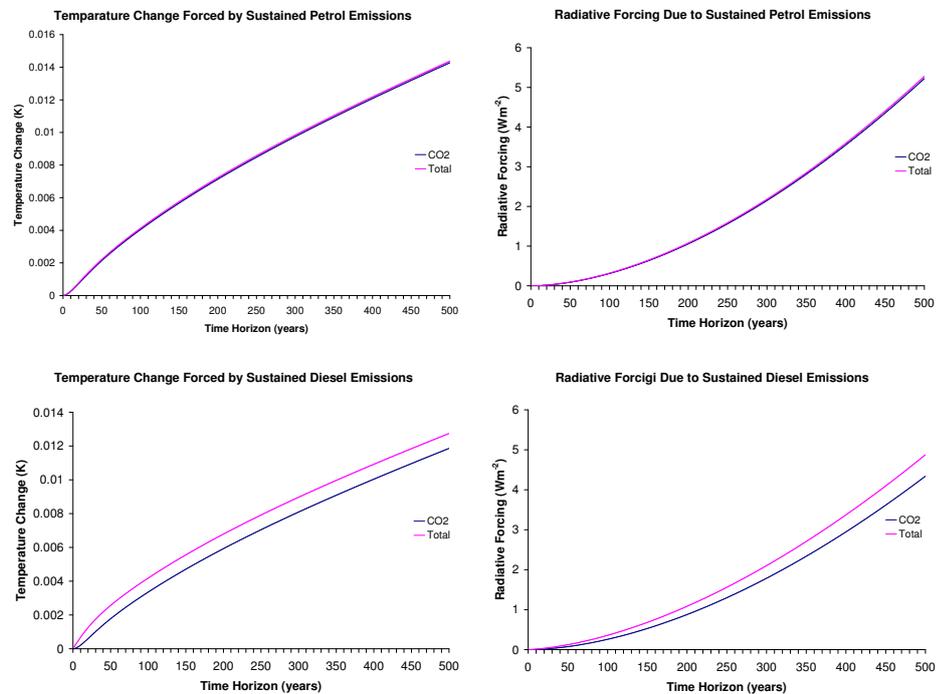
**Figure 22:** Comparison of the impact due to total sustained emissions to that due to $CO_2$
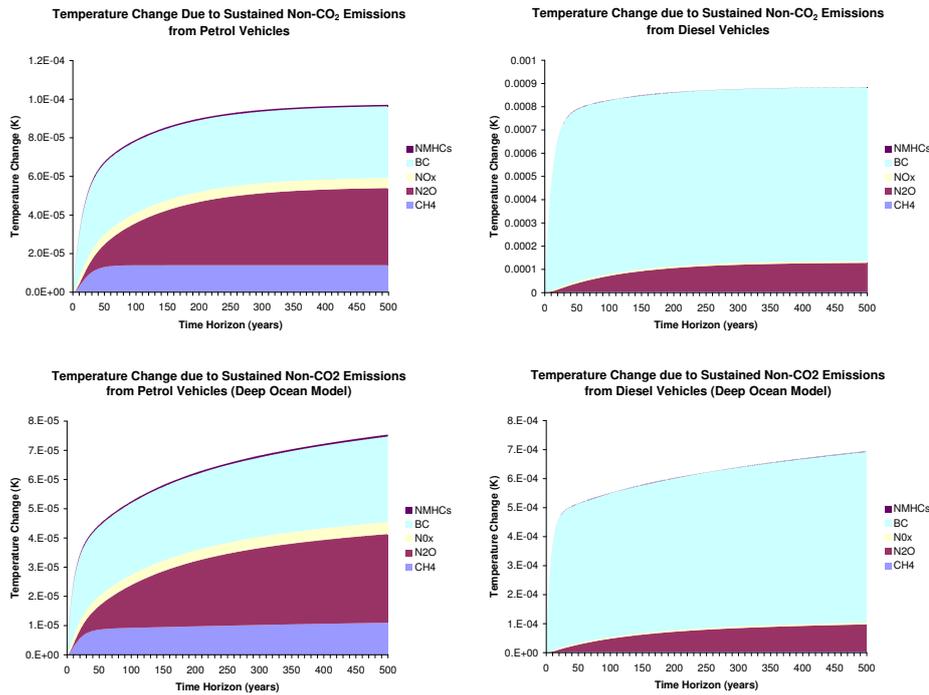
**Figure 23:** Global temperature change contribution of non-$CO_2$ constituents of vehicle emissions (stacked) as modelled by both the simple and deep ocean models

have a greater impact (an order of magnitude higher than for petrol), mainly as a result of BC emissions. Recalling that BC forces a large temperature change initially, we can associate it with the initially larger temperature change by diesel vehicles compares to fuel vehicles (figure 21). With the phasing out of vehicles without particulate filters, we expect that the temperature change due to diesel vehicles will be lower in magnitude and drop below that due to petrol vehicles within a shorter period than the 110 years for sustained 2002 emissions.

Technology is also in place to reduce $NO_x$ emission (catalysts). Figure 24 we can see that diesel vehicles are having a higher impact due to $NO_x$ emissions. Therefore diesel vehicles stand to have a higher benefit from this technology.

The effect of NMHC is low for both fuel types. However, comparing the
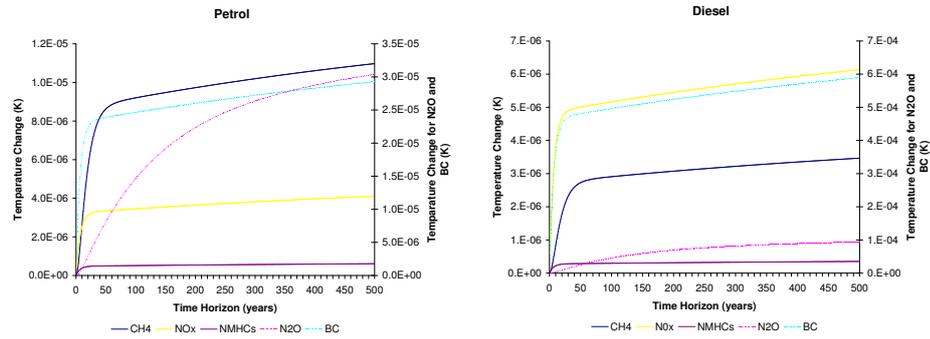
**Figure 24:** Global temperature change contribution of non-CO$_2$ constituents of sustained vehicle emissions as modelled by the deep ocean model
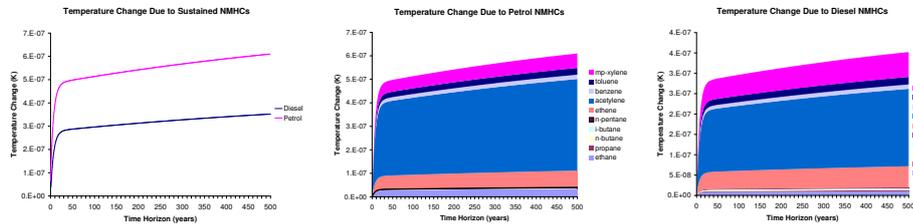


**Figure 25:** Temperature change due to sustained NHMC emissions (deep ocean model)

two fuel types, the NMHC impact due to petrol vehicles is almost double that due to diesel vehicles. The difference between the emissions from the two fuel types is even larger, recalling that 80% of the petrol NMHC emissions are unaccounted for, compared to 32% for diesel. The total forcing due to the NMHCs is could also be larger, if indeed the perturbation times have been under estimated.

From figure 25, the NMHC to target if we are to reduce the impact of NMHCs is acetylene, whose high impact is mainly due to high per kg impact rather than high emission volumes. Ethene and m+p xylene, with the high radiative efficiencies, are also a major contributors.

We were unable to assess the impacts of carbon monoxide due to the unavailability of data disaggregated according to fuel types. However this should not have a large effect on decision making as the radiative efficiency

of CO is low, with a GWP of about 1, i.e almost has the warming potential as $CO_2$ . The CO emissions are however much lower than those for $CO_2$. According to Biggott et al. (2007) the CO emissions for road transportation (UK) is $1.85 \times 10^9$ kg compared to $1.19 \times 10^{11}$ kg for $CO_2$.

## 5.2   Per km Emissions

In order to make a conclusion on which fuel type is to be used if we are to minimize the impact of road transportation emissions on the climate, while considering environmental impacts we need to consider per km emissions. This is because comparing emissions for the whole fleet, as done in the previous section needs to take into account market-share changes, which have not been inclued in the metrics. One way to include them would be through incorporating them into the emission rate, $\Delta S(t)$. But this is already a complex parameter.

We divide the emissions by vehicle kilometers; $3.48 \times 10^{11}$ vehicle km for petrol and $1.38 \times 10^{11}$ vehicle km for diesel vehicles (Department for Transport (2003)). Within the time constraints of this project we were not able to perform a thorough analysis in this regard. However, considering $CO_2$ emissions which have the greatest impact we find that the diesel vehicles are actually having higher $CO_2$ emissions per km than their petrol counterparts (388g per diesel km versus 185g per petrol km). This implies that promoting diesel vehicles would not only increase the emissions of non-$CO_2$ emissions such as BC, which have adverse effects on environmental health, but would also have an overall increase on the climate impact. This is contrary to expectations as, despite diesel having a higher carbon content, diesel engine efficiency is sufficiently high. This means that diesel vehicles burn less diesel per km, and should therefore have lower carbon emissions per km.

We suppose that this discrepency could be as a result of the errors in either the emission factors or vehicle km.

# 6   Conclusions and Areas of Further Work

This dissertation found that the deep ocean could help slow down the impacts of emissions on the climate system. This is achieved as the ocean has some mechanisms such as diffusion and downwelling/upwelling that tranfer water and energy across the thermocline.

We also found that in the UK, 2002, petrol vehicles had higher emissions (by mass) than their diesel counterparts. This corresponds to a higher instantaneous radiative forcing for diesel, resulting from the fact that diesel emissions contain a higher proportion of short-lived emissions with a high radiative efficiency (BC). However because of the short-lifetime, when considering exponential decay of the radiative forcing we found that petrol emissions actually have a higher radiative efficiency.

The temperature change resulting from these emissions is such that during the first few decades the change due to diesel emissions is higher than that due to petrol emissions. However the introduction of diesel particulate filters is expected to change this, leaving the impact of diesel emissions lower through out.

Technologies that reduce emissions (particulate filters and catalyst) have been observed to have a negative impact on energy efficiency, therefore reduce other emissions at the expense of $CO_2$, with some catalysts achieving their goal by oxygenising carbonaceous emissions into $CO_2$. This achieves air quality objectives, but from a climate change perspective there is a need to quantify the benefits of eliminating the non-$CO_2$ emissions and against the additional forcing due to the increased $CO_2$ emissions. In order to achieve this there will be need to more accurately quantify all the emissions that are reduced by the technologies, including NMHCs. This, therefore, calls

for a study to develop more accurate emission factors and lifetimes for the NMHCs.

Finding disaggregated data was not an easy task. However, in order to quantify and compare the overall global impact of petrol and road transportation, there is a need to disaggregate global road transportation data into its petrol and diesel constituents. Once this is done, there would then be need to be careful in dealing with emissions such as $NO_x$, whose emission factors are regional.

Another area of concern is the per kilometer emissions and their impacts. There is need to assess in further detail how the estimations for the emissions were derived, assessing whether they are based on the same fleet volume and vehicle kilometers as reported by the Department for Transport.

Based on the amount of work that is still required, this dissartation can not come to a conclusion as to which is the better between petrol and diesel vehicles. However, we do acknowledge that diesel vehicles currently have measures in place to substantially reduce their non-$CO_2$ emission constituents.

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